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**Evaluation of Final Waste Forms and
Recommendations for Baseline
Alternatives to Grout and Glass**

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MANAGED AND OPERATED BY
LOCKHEED MARTIN ENERGY RESEARCH CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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Chemical Technology Division

**EVALUATION OF FINAL WASTE FORMS AND RECOMMENDATIONS
FOR BASELINE ALTERNATIVES TO GROUT AND GLASS**

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PREFACE

Grout and glass waste forms are two materials around which baseline technologies have been built for the stabilization and solidification (S/S) of hazardous, radioactive, and mixed wastes. These materials have served these needs with varying degrees of success. Grout has been the most widely adapted waste form, being used to treat many types of wastes. On the other hand, the use of glass waste forms has been relatively limited, being essentially restricted to radioactive wastes.

Some of the more troublesome of voluminous wastes within the Department of Energy (DOE) complex are those that contain the metals identified by the Resource Conservation and Recovery Act (RCRA) as hazardous. These metals are often problematic for grout-based and glass-based technologies, and the technical problems associated with these RCRA metals can be especially acute for mixed, hazardous, and radioactive wastes, such as those on the Oak Ridge Reservation (ORR). These considerations make the design of suitable criteria by which to assess and to regulate the S/S of such wastes suspect and, thereby, limit the development of better predictive capabilities of waste-form performance for grout and glass.

This condition is exacerbated by the common perception that one or two waste forms are suitable for the wide variety of hazardous and mixed wastes that must be treated. Experience demonstrates otherwise. Indeed, some of the waste problems persist after many years of technological development for grout-based and glass-based waste forms. Hence, it is timely to examine the technical bases by which these waste forms perform, in order to gain perspective on their most limiting characteristics and remaining technological hurdles. Similarly, it is appropriate to identify and to understand the collective status of alternative materials and technologies. To a large extent, the advantages and disadvantages of potential alternatives, such as polyethylene, bitumens, sulfur, and crystalline ceramics, to name a few, are known only qualitatively and without a critical understanding of the inherent similarities and differences that each has relative to the two baseline materials, grout and glass.

Moreover, current perceptions of these and other alternatives are based, in part, on the economic aspects of production and normally tend to neglect the economics of performance over the lifetime of storage and burial, including the costs demanded by the mandated monitoring of waste burial sites. In other

words, short-term considerations often skew the assessment of the long-term technical properties which would ensure cost-effective S/S of hazardous and mixed wastes of the DOE.

The present report attempts to pull diverse areas of waste-form technologies together. Specifically, a foundation is established herein that provides insight on both how waste forms operate and the nature of their limiting characteristics. The general principles that are shared by the various waste forms are identified. Analogously, the absolute and relative traits that help to set individual waste-form behavior are revealed. These are mostly grounded in the chemical and microstructural characteristics of each waste form. Based on the technical literature, the report examines grout and silica glasses as baseline materials, whereas it treats bitumen, sulfur, and polyethylene, for example, as materials that exemplify the common alternative behavior desired.

The structure of the report permits separate topics to be easily identified. Following the Introduction, Sect. 3 describes the various waste forms generically. Sections 4 and 5 discuss relevant regulatory issues and the central concept that waste and waste-forms matrices must be considered together. Each presents unique chemical or compositional issues, and each can influence the processing methods used. Moreover, either can dominate the microstructure that develops during processing, essentially setting the success with which hazardous and radioactive components are solidified and stabilized.

Sections 6 and 7 address the relative properties of wastes and waste forms, emphasizing studies that have been conducted using actual waste. The scale of these studies extends from laboratory to full scale. Finally, Sect. 8 pulls the various aspects together in order to present general and specific recommendations. The attractiveness of certain waste-form technologies as short-term solutions for problematic wastes and their inadequacies for long-term uses are identified. The desirability of thermodynamic stability for the final waste-matrix system suggests that heretofore discounted waste-form technologies, based on glass-ceramics and ceramic systems, ought to be developed for the most troublesome hazardous, radioactive, and mixed wastes. These concepts are discussed in terms of assessing the various technological alternatives.

The extensive bibliography was constructed in a fashion that permits a variety of audiences to pursue the technical literature. The general background; programmatic literature; information on the symbols,

terms, and nomenclature used herein; and references on specific waste forms are grouped in a fashion that permits a directed search of the issues discussed in the body of the report. A detailed glossary contains an overview of the important symbols, terms, and nomenclature. Lastly, tables and figures are constructed in a manner to maximize their stand-alone qualities.

1. ABSTRACT

An assessment of final waste forms was made as part of the Federal Facilities Compliance Agreement/Development, Demonstration, Testing, and Evaluation (FFCA/DDT&E) Program because supplemental waste-form technologies are needed for the hazardous, radioactive, and mixed wastes of concern to the Department of Energy and the problematic wastes on the Oak Ridge Reservation. The principal objective was to identify a primary waste-form candidate as an alternative to grout (cement) and glass.

The effort principally comprised a literature search, the goal of which was to establish a knowledge base regarding four areas: (1) the waste-form technologies based on grout and glass, (2) candidate alternatives, (3) the wastes that need to be immobilized, and (4) the technical and regulatory constraints on the waste-form technologies. This report serves, in part, to meet this goal.

Six families of materials emerged as relevant: inorganic, organic, vitrified, devitrified, ceramic, and metallic matrices. Multiple members of each family were assessed, emphasizing the materials-oriented factors and accounting for the fact that the two most prevalent types of waste for the FFCA/DDT&E Program are aqueous liquids and inorganic sludges and solids.

Presently, no individual matrix is sufficiently developed to permit its immediate implementation as a baseline alternative. Three thermoplastic materials, sulfur-polymer cement (inorganic), bitumen (organic), and polyethylene (organic), are the most technologically developed candidates. Each warrants further study, emphasizing the engineering and economic factors, but each also has limitations that relegate it to a status of short-term alternative. The crystallinity and flexible processing of sulfur provide sulfur-polymer cement with the highest potential for short-term success via encapsulation.

Long-term immobilization demands chemical stabilization, which the thermoplastic matrices do not offer. Among the properties of the remaining candidates, those of glass-ceramics (devitrified matrices) represent the best compromise for meeting the probable stricter disposal requirements in the future.

2. INTRODUCTION

The Development, Demonstration, Testing, and Evaluation (DDT&E) Program [325] is evaluating multiple technologies for their abilities to treat mixed wastes and to reduce the hazardous constituents to suitable levels for land disposal in compliance with the Land Disposal Restrictions (LDR) of the Resource Conservation and Recovery Act (RCRA) [268,360,361,362,363,364]. Two principal technologies under evaluation are Final Waste Forms (Solidification/Stabilization Technologies) and Thermal Treatment. The program focuses on cement-based (i.e., grout) technology as the baseline technology for Final Waste Forms. Grout was selected as the principal option for several reasons: (1) it is the most widely used waste-form technology for the treatment of hazardous, radioactive, and mixed wastes; (2) commercial grout processes are readily available; (3) grout has a proven history or track record; (4) grout is specified by the Environmental Protection Agency (EPA) as the best demonstrated available technology (BDAT) [354,363] for a few select wastes; and (5) owing to the foregoing reasons, grout technology can be implemented to treat waste in a timely manner, in order to meet program schedule constraints.

As an alternative to grout, the program is also evaluating vitrification technology as a second priority. Vitrification (i.e., the making of glass) was selected primarily in view of the fact that the DDT&E Program assumes that no single waste form will adequately treat wastes containing significant concentrations of organic constituents; that is, it is assumed that the waste will have undergone thermal treatment in order to remove organics and, possibly, other constituents and that the residue from the thermal treatment will have been evaluated prior to its stabilization/solidification (S/S). Vitrification is the primary alternative to grout because it offers the potential to perform both the thermal treatment and to solidify the resulting residue in one processing step. In view of the fact that vitrification is the baseline waste-form technology for high-level radioactive wastes, the data base generated in developing the technology for those wastes seems applicable to the S/S of mixed wastes.

Experience with grout processes, which are the most widely used S/S processes, has clearly shown that the subject of waste-form performance is complex. It is a function of the feed characteristics, the waste-form matrix material, the chemical interactions between the waste and the waste-form matrix, the processing history, and the final handling and storage conditions. Recognizing these complexities, most

researchers have attempted to simplify the chemistry between the waste and the waste-form matrix materials. This step has been most often accomplished by developing solidification processes that primarily encapsulate the waste,¹ rather than by seeking stabilization processes that rely on the chemical conversion of waste species into more environmentally stable (acceptable) forms.² Indeed, most alternatives to grout technology (e.g., technologies for glass, thermoplastics, and thermosets) chiefly promote encapsulation.

This report provides recommendations for the alternative waste forms to grout and glass, recognizing that no single waste form is optimum for all types of waste. Moreover, it is based on the recognition that both stabilization and encapsulation processes are complex and that the selection of the best waste form involves numerous issues which are described herein.

2.1. Scope of Evaluation

The literature search that underpins this report and the report itself have been directed toward two major objectives: to provide direction for alternative treatability studies and to elucidate significant engineering requirements for a potential waste-form alternative to grout and glass. Four principal assumptions were adopted at the outset of this effort. (1) The best long-term waste-form properties will demand that the majority of hazardous and mixed wastes of concern be stabilized. In turn, immobilization mechanisms are fundamentally more suitable than encapsulation mechanisms. (2) The technical (i.e., scientific and engineering) aspects of competing technologies need to be assessed before the cost assignments for subsets of the recommended waste form technology schemes can be considered. Thus, the issues of cost are not to be considered, per se, at this time. (3) The final waste forms are destined for shallow land disposal. Under these conditions, the probability that the buried waste form will be exposed to water is high. If the various physical and chemical interactions of water with the waste form and the waste are

¹Encapsulation is the enclosure of hazardous, radioactive, or mixed waste in a solid waste form, such that the waste exists as (a) microscopic particulates (microencapsulation), (b) particulates contained within or coated with an impervious layer that is distinct from the matrix material (macroencapsulation), or (c) macroscopic particulates and solids embedded in a solid waste-form matrix (embedment). The resultant waste form is composed of multiple phases.

²Stabilization is the reduction of the hazard potential of a waste by chemically converting the contaminants into their least soluble, mobile, or toxic form. The resultant waste form may be either single phase or composed of multiple phases.

detrimental to the long-term land disposal of the waste, the implications of shallow land disposal must be considered in this regard. (4) The relative importance of a given waste form is primarily affected by its ability to immobilize a given type of waste. The relative abundance of the waste is of secondary or lower priority and, as such, does not affect the present evaluation of the specific waste-form technologies described herein. Consequently, the recommendations offered in this report reflect the technical requirements of individual types of waste and the technical suitability of available final waste forms. They do not reflect the relative quantities of individual wastes for which disposal is needed.

2.2. The Need for Alternatives

Cement-based and glass-based waste forms exhibit many attractive properties that are important, if not critical, for the successful use of stabilization and solidification procedures. Among the attributes of cement-based waste forms are the generally ready availability of the chemical ingredients, the adaptability of cement compositions to accommodate various types of waste, the combination of acceptable mechanical properties and low weight, the relative ease of processing under ambient conditions of temperature and pressure, and the general resistance to attack by water, UV-radiation, and biological organisms. Analogously, the attributes of glass-based waste forms are multifold. They include the use of commonly available chemical ingredients, acceptable mechanical properties, and the flexibility of chemical composition that can be tailored to incorporate a variety of wastes.

2.2.1. Grout

Grout, a cement-based waste form, has proven successful in many waste S/S applications, including recent ones for mixed waste [389] and radioactive wastes [388,390,398]. Some of these successes are based on the collective technical expertise on cement and concrete that has evolved after many years of study for the purposes of waste disposal and other operations. Much of the research on these materials that supports the implementation of grout technology relies on careful analyses of the compositional and microstructural features of the waste-free and waste-containing matrices.

Notwithstanding the successes, some problems exist and limit the usefulness of grout for the S/S of hazardous, radioactive, and mixed wastes. Some stem from the fact that grout is inadequate for a large

number of wastes [337]. For instance, some important wastes can be leached too readily from grout; these include wastes that contain radionuclides [395] or volatile organic compounds [397]. Also, the occurrence of incomplete chemical reactions (viz., hydrolysis) in grout can lead to detrimental, time-dependent, leaching behavior, and the hydration of grout can be critically inhibited or stopped altogether under ambient conditions by some waste species (e.g., organics). Still, other wastes (e.g., some specific metals and anions) can negatively affect the processing of grout, making the setting process difficult at best.

It is noteworthy that the cement-based grout matrix contains a complex porous microstructure and that some undesirable leaching properties relate both to it and to the liquid within it. Also, the porosity can lead to an unacceptably large bulk volume of material that must be handled, stored, and buried. This situation reflects an important materials issue: namely, other waste forms, such as sulfur-polymer cement, organic thermosetting resins and thermoplastic polymers, glass, glass-ceramics, and ceramics, can be made to have significantly less specific bulk volume than that for grout waste forms. This relatively reduced specific bulk volume results, in part, from the fact that these waste forms are not greatly porous. Hence, in addition to the scale of the handling, storing, and disposing of grout-based waste forms, the economics related to the increased volume for disposal can be unacceptably high, making the alternative forms more attractive. Until analogous data are available for alternatives, the assessment of the economics for an individual waste form cannot be fully addressed.

Engineering concerns also exist. Some focus on the time-consuming shutdown process for grout. Others focus on the fact that wastes which contain organic constituents can be pretreated (e.g., via thermal desorption [164]) in order to remove these components. In this case, the pretreatment also removes any water that coexisted in the waste, a result which demands that water be readded in order to solidify and stabilize the hazardous residue in grout.

This status leads to the conclusion that alternatives to grout are desirable in order to circumvent its inherent limitations and those of its technology. Some of these problems are successfully resolved by the implementation of a technology that uses glass waste forms.

2.2.2. Glass

Vitrification has been examined in great detail for the stabilization and solidification of radioactive wastes, especially high-level wastes [254,436,439,442,443,452,466,468]. Successful applications have been achieved with borosilicate glasses (i.e., SiO_2 glasses that contain approximately 80 wt % SiO_2 and 13 to 15 wt % boron oxide, B_2O_3 [180]). In some cases, the efforts have led to the development of pilot-scale or full-scale operations [441,445,448,455,459,466,468].

Contrasting the abundance of research that has been conducted on glass waste forms for high-level wastes, relatively little attention has been paid to the use of glass waste forms for hazardous and mixed waste [278]. Therefore, a general lack of information for the application of vitrification techniques to the treatment and disposal of hazardous and mixed wastes exists. Thus, although glass has the potential for adequately encapsulating many RCRA metals, the achievements realized for high-level wastes have yet to be demonstrated for the wide variety of hazardous and mixed wastes.

Alternatively, the present status of glass research does not yet permit glass waste forms to be tailored for the wide range of wastes that must be treated. As a result, problematic wastes exist. These include highly saline wastes, some of which liberate acidic off-gases during the vitrification process. These gases require scrubbers and related equipment in order to eliminate their release to the environment. Many waste species have limited solubility in glass. Also, only limited data on the applicability of glass to hazardous and mixed wastes have been gathered; examples might include metal plating waste (Ni, Cr). For these applications, the durability of glass waste forms has not been adequately demonstrated.

2.2.3. General Considerations

The limitations for grout and glass are critical. They underscore the present general inability to meet the current and near-future regulatory requirements regarding the properties of stabilized and solidified hazardous and low-level wastes. Many of these requirements are reviewed in the ensuing discussion. In view of the facts that each type of regulated waste must be suitably solidified and stabilized prior to disposal and that cement-based and glass-based waste forms cannot acceptably meet the requirements for all types of hazardous and low-level wastes, the current assessment is that alternative waste forms

need to be identified. The observation that the chemical interactions between the waste species and the matrix are normally complex underscores this need. Although exceptions exist, these interactions are not understood well, and, therefore, they are not readily controlled with grout and glass waste forms.

The foregoing considerations also reinforce the more important conclusion that no single waste form is likely to be suitable for each type of waste. Three important implications follow from this concept: (1) the chemical and physical properties of each hazardous waste stream establish the technical requirements of acceptable candidate waste forms; (2) the properties of the candidate waste forms, in turn, set the relative priority that should be associated with each potential waste form; and (3) the issues of cost only apply to those waste forms that survive the assignment of technical priorities for each type of waste. This last implication directly follows from the regulatory status, as described in the following section: that is, each type of waste must be treated for disposal. Furthermore, only those wastes for which no acceptable incineration, stabilization, or solidification technology exists may be stored.

Consequently, the subject evaluations for this report and the development of suitable recommendations are primarily driven by the chemical and physical nature of the wastes to be treated for disposal. Specific factors that justify the selection of a specific final waste form (FWF) include its time-dependent properties, which impinge on the anticipated lifetime of the FWF; the degree of shielding required; the containment specifications; and the type of handling that the FWF is to undergo [353,358].

A main consideration for a suitable final waste form is whether or not disposal is imminent. If it is not, an interim storage period is required, and this duration can be as long as 50 years [358]. Such concerns are generally evident in regard to low-level radioactive wastes that are generated in a nuclear fuel cycle. They are also relevant to the disposal of hazardous and radioactive wastes generated in medical, industrial, and research applications [146,148,255,257].

The foregoing concepts lead to the conclusion that an evaluation of the available waste forms must be undertaken in order to identify a suitable "best" alternative waste form to grout and glass. This process is under way, and the present report constitutes one of its first steps. The concepts and recommendations contained in it are offered as working tenets to be assessed and refined as needed. It is hoped that this report addresses some needs within individual programs; helps to elucidate important relationships

among programs, irrespective of whether or not formal ties presently exist; and comprises a relevant collection of fundamental concepts with which research and development needs can be better identified and addressed.

2.3. Regulatory Considerations

Numerous regulations may apply to the waste forms that result from the treatment of mixed wastes. The most important of these regulatory requirements and constraints relate to the LDR of RCRA. Although they have been recently discussed in detail [329], these regulations are briefly addressed here in order to promote an understanding of their impact on the recommendations provided in this report.

An overriding general assumption is that the hazardous waste is properly identified before the principles described herein are applied; that is, the following conditions are assumed to be met for the wastes considered by this study: (1) the waste is solid; (2) it is not exempted from regulations established under RCRA; and (3) it is a declared, listed, or characteristic hazardous waste. If any of these is not met, the "waste" is not subject to RCRA regulations and is not part of the DDT&E Program.

For the present purposes, a waste is first and foremost a material that is to be discarded. It is also a hazard if it has the added potential for causing harm to human health or to the environment [265,356]. Although acts such as Occupational Safety and Health Act (OSHA) may regulate the material's use, its pretreatment, if needed, and disposal are regulated under RCRA. The proper classification of a waste that it is hazardous is set by the various properties which the waste exhibits. If its properties reveal it to be a member of any waste types described in Table III, the waste is regulated under RCRA and related acts as a hazardous waste [348k,360,363,365]. Conversely, if it does not exhibit the properties given in this table, the waste is not subject to regulations under RCRA as a hazardous waste, unless the generator declares it so.

A simple example demonstrates that this distinction may be critical in practice. Consider two waste streams that are nearly identical. The first is hazardous solely because its pH value is 1.8, and it is regulated under RCRA as hazardous waste, owing to its corrosive character (see Table III). If the second stream has a pH value of 2.2, which exceeds the acidic limit given in the table, and its properties are

otherwise identical to those of the first stream, the second waste stream is not hazardous waste, according to RCRA. Its disposal is not regulated as such under RCRA. If this subtle difference in properties is overlooked, the total volume of hazardous waste to be treated for disposal is unnecessarily high.

Four general types of hazardous waste exist, according to the classification systems adopted under RCRA. The major traits that these types possess are summarized in Table III. As this table reveals, a waste may simply be declared to be hazardous. This declaration is usually based on the generator's experience with the waste components [363]. Sometimes, inadequate knowledge leads a generator to declare a waste as hazardous, owing either to the lack of adequate chemical or physical analyses or to ignorance regarding the limited types of materials that are regulated under RCRA [365]. Characteristic wastes exhibit any of the four traits in Table III: low-temperature ignitability, corrosiveness, explosive or violent chemical reactivity, and toxicity [265]. Acutely toxic wastes are listed as a separate category under RCRA and related acts.

Whereas the traits and comments in Table III are useful for describing the types of hazardous waste, they do not provide information about the specific chemical nature and their physical forms that would generally permit decisions regarding waste forms. These aspects are summarized by the generic categories of waste listed in Table IV. The general properties and some representative examples of the members within each category are also given in the table in order to provide a perspective by which the composition of waste may be classified. These categories exhibit the breadth of wastes that may be encountered. Assignment of a specific waste to one of these categories is relatively straightforward, at least in principle, if the waste is sufficiently analyzed and its properties are assessed. However, an assessment may be difficult because the available quantitative data are limited or adequate qualitative knowledge about the waste is unavailable.

Another approach by which hazardous wastes may be classified is according to the impact that their physical and chemical properties have on their treatment, solidification, and various disposal procedures [331]. These properties help to set physical limitations within which various processes must be designed. For example, whether or not a waste can be transported through a treatment process (i.e., say the ease or difficulty with which it can be pumped in contrast to other transport procedures) depends

critically on its physical form and the chemical problems associated with it. Clearly, the chemical and physical properties of the waste also affect the chemical approaches by which the waste is made nonhazardous. This step may be accomplished by destruction of the waste, by removing its hazardous constituents, which likely generates another batch of waste, or by immobilization and solidification [331]. Generally, these considerations focus on the processing that the waste undergoes.

The classification scheme in Table V provides the assignment of hazardous wastes with this emphasis, according to the Department of Energy (DOE) [331]. These categories are discussed in detail in Sect. 4. Consequently, at this point, it suffices to note that the members of the categories—aqueous liquids, organic liquids, organic sludges and solids, inorganic sludges and solids, and debris—essentially match those in some of the categories in Table IV. However, the wastes in the other categories in Table V, when processing is considered, do not match those grouped together in Table IV, when the properties of the waste are considered without regard to their impact on processing.

Specific wastes that belong to the groups identified in Table V which are of particular concern for the DDT&E Program are summarized in Table VI. The data in this table reflect a recent effort of the DOE to identify the 1478 waste streams that are presently stored at its 50 sites distributed over 22 states. The estimated volume of this stored waste is approximately 581,810 m³, according to the data in Table VI. The inventory is expected to grow by another 50 vol % over the next 5 years [331], that is, after neglecting the additional volume that would be generated as a result of various waste stream activities. Only approximately 40 vol % of the total quantity of waste that is presently stored is treatable via existing treatment technologies. Hence, the remainder, viz., 60 vol % of the currently stored waste, demands that either modifications to existing waste-form technology be made or that new waste-form technologies be developed. Of the types of waste included in Table VI, the three most prevalent are aqueous liquids, inorganic solids, and debris [330]. These categories are described in Sect. 4, and the general problems associated with their respective wastes, including their impact on the assessment of alternative waste forms, are addressed in Sect. 6.

Some existing constraints apply to the selection of potential candidate technologies and waste forms to be considered. The most pertinent ones are listed in Table I. The relevance of these limitations on the present evaluation process is used as a qualitative measure of their relative importance. Compliance with

federal and state regulations is deemed the most critical constraint. The desirability of large-scale processes, minimized health and safety risks, the ability to accommodate numerous types of waste, and the relative supremacy of stabilization over solidification are then considered to be preferred attributes. Obviously, a given technology or waste form may not meet all these criteria. In that case, a ranking of waste-form properties is needed. This ranking and its implications are also discussed herein.

The focus of this report is to help meet the Land Disposal Restrictions (LDR) of the Resource Conservation and Recovery Act (RCRA) [360,362,363,364,370], as Sect. 3 describes. The literature on pertinent aspects of these regulations is certainly huge and includes reports, journal articles, and contributions to proceedings of meetings. The technical literature on available final waste-form technologies is similarly vast, irrespective of whether large-scale commercial and nearly commercial operations are considered or exploratory, fundamental research and development is desired. Consequently, the literature search conducted for the present evaluation covers these many sources, and it focuses, in part, on the technical mechanisms upon which the available waste-form technologies and those which are likely to be available in the near future are based. Examples of these mechanisms are chemical fixation, solidification, sorption, and gelation. Important potential matrices (i.e., final waste forms) that are considered in this study are advanced vitrified glass, devitrified inorganic glasses (i.e., glass-ceramics), thermoplastic organic polymers and sulfur-polymer cement, and ceramics. Cementitious matrices (e.g., portland cement and grout) [23,30,46,391] and common vitrified glasses (e.g., borosilicate glass) [124] are also included in this study for the purpose of comparing their technical and nontechnical features with those of the leading potential alternative final waste forms.

An equally important objective of the search is to establish an acceptable perspective on the overall set of problems associated with the Federal Facilities Compliance Act (FFCA) [347] and the research efforts and related programs [323,325] that address the wastes generated or stored at the Oak Ridge Reservation (ORR). These wastes are summarized in Table VI. The Development, Demonstration, Testing, and Evaluation (DDT&E) Program is particularly relevant [325]. It has a deadline of March 1995 for the delivery of a treatability methods plan. The establishment of the Mixed Waste Treatment Facility (MWTF) is another effort [325] that the present evaluation process strives to impact. This facility could provide the treatment capability and capacity for the treatment of mixed waste for ultimate disposal [326].

This need for a useful perspective for integrated solutions to disparate efforts at ORR is one which is typically met by hands-on experience. However, the time that is available to meet this need does not allow for such an approach. Still, an understanding of the prevalent types of wastes, the generic aspects of relevant approaches already tried, irrespective of their technical success and sociopolitical implications, the spirit and context of FFCA, and the operating premises adopted by Lockheed Martin Energy Systems (LMES) must be assessed without emphasizing any single aspect or any small combination of them unduly. Hence, a balanced perspective can be developed in order to best evaluate the limitations of currently used final waste-form technologies. Then, the steps and procedures that must be implemented to pursue appropriate alternatives can be developed. Only with an appreciation of these areas is it possible to generate a useful compilation of alternatives to grout and glass and to ascribe a reasonable ranking to them. In order to accomplish this task and to identify the "best" routes to accomplish the goals of this study as quickly as is feasible, various sources were consulted. These displayed diverse viewpoints, as the summary in Table II reveals.

2.4. Waste-Form Microstructure

A final specimen that is destined to be treated for disposal is not usually a homogeneous solid solution. It has a microstructure that generally reveals combinations of the following characteristics: chemical and physical heterogeneity that distinguishes concentrated regions of waste and host matrix, porosity, nonuniform distribution of the waste species in the bulk of the matrix, and grain boundaries and surfaces that are rich in some waste species while being depleted of others. Consequently, the properties of specific waste forms and their ability to meet various performance criteria derive from a complex set of conditions and phenomena. This situation is somewhat understood for virtually every type of waste form envisioned. However, the present state of knowledge for each waste form is seriously deficient in critical areas, and this limitation makes the prediction of behavior for the waste-matrix combination increasingly difficult, if not superficial, as the regulatory and other desirable goals become more demanding.

The performance of specific final waste forms (FWF) can be best understood in terms of their chemistry, the processing by which they are fabricated, the microstructure that exists within the FWF, and the properties that contribute to performance of what is typically a composite system. The chemical focal points are the composition and physical state (e.g., degree of miscibility and degree of subdivision of

solid, liquid, and gaseous components) of the starting materials and the chemical reactivity that the starting materials may exhibit. Various fabrication schemes are usually possible. The selection of the most desirable ones and the setting of process variables and conditions combine to establish the processing history that the final waste-matrix specimens experience. The chemistry of the original systems and their processing history lead, in turn, to the development of microstructures that underpin the properties that the components exhibit. Consider one example, the density of the final, waste-matrix system. When expressed as a fraction of the theoretical density that corresponds to the final solidified mixture, the density provides an estimate of the degree of porosity. However, whether or not this porosity is important in the performance of the waste-matrix system depends much more critically on the specific arrangement of pores, their size, their continuity, and the properties of the solid phases that stabilize them, among other factors; that is, the microstructural features establish the effect that the porosity has on the physical properties that combine to provide the observed performance.

This principle can be extended to any pair of microstructural feature and final property. Consequently, the concept that the microstructure of the waste-free and waste-loaded matrices determines their properties is central to the present report and underscores the discussions on materials behavior and processing. The microstructure depends, in turn, on two factors already mentioned. These are the composition of the starting materials and the physicochemical aspects of the processing scheme used to fabricate the waste-matrix system that the specimens actually experience. Therefore, the chemistry involved in the preparation of the waste forms, the processing behavior of these systems, the microstructure of the final waste forms, and the properties of the solidified waste forms clearly constitute the essence of the technical features of each waste form considered. The overriding principles by which these factors affect waste-form performance are stressed herein.

3. CANDIDATE MATERIALS AND RELEVANT PROCESSING CONCEPTS

Numerous materials have been developed to serve as final waste forms for radioactive and hazardous wastes. The variety of these systems that have been developed as matrices for this purpose is broad and is summarized in Table VII. The compositions and microstructures of these matrices lead to the classifications used in the table. The six major families in this scheme consist of inorganic, organic, vitrified, devitrified, ceramic, and metallic materials. These classifications are set somewhat arbitrarily, but they are useful and instructive for the present purposes. Alternatively, the materials systems described herein can be assigned to fewer categories, viz., the four that are widely used outside the waste disposal community: ceramics, polymers, metals, and composites. Although the benefits of such a classification include a more consistent set of materials issues (e.g., microstructural concerns), the semantic limitations posed by these four classes are too severe for the present purposes.

The present section describes the principal members of each family listed in Table VII. The commonly used raw materials or starting components are given. Then, the general chemical and physical principles that support the primary technologies which have been developed for each family are described. These principles are discussed in a manner that emphasizes (1) the processing (i.e., fabrication techniques) of the principal member of each family, (2) the development of relevant microstructures in these materials and their common variants, and (3) the properties which ultimately ensure the usefulness of these matrices in the waste-disposal applications envisioned herein. Especially important are the interrelationships among the chemistry involved, the processing techniques used, the microstructures developed, and the final matrix properties that emerge from such a discussion: that is, the evolutionary manner by which the chemistry and the processing scheme combine to dictate the microstructure that develops within a matrix and the dependence of the final matrix properties on that microstructure are deemed crucial to the performance of the final-waste-form matrix as a stabilization and solidification system for radioactive, hazardous, and mixed wastes.

The mastery of these interrelationships is essential both to the optimization of performance for wastes that are currently stabilized, solidified, and otherwise treated for disposal and to the development of advanced waste forms for the wastes that are not satisfactorily addressed at the present time. Consequently, the clarification of the generic chemistry-processing-microstructure-property relationships

that underpin the relevant properties of the currently used waste-form matrices and of the proposed candidate matrices is an important feature of the rationale used herein. This protocol helps to identify and to assess the most important systems listed in Table VII in an efficient manner. Moreover, an understanding of these relationships and an appreciation of their importance to performance criteria are critical both to the assessment of final waste forms and the recommendation of alternatives to grout and glass. As new developments emerge, they can be incorporated into this framework, and the relative status of our ability to handle a variety of wastes will improve.

Although the use of the principal materials in Table VII as final waste forms is the primary driving force for the present discussion, the matrices themselves (i.e., waste-free matrices) are the focal points in this section. The incorporation of waste into them and the concomitant effects on relevant chemistry-processing-microstructure-property relationships are described in Sect. 5. This approach ensures that the importance of the interrelationships among the chemical, processing, microstructural, and property aspects is developed for the principal systems within each family. Then, the dominating role that these interrelationships play in establishing the degree of success with which final-waste-form matrices can be developed will become evident (i.e., in a manner by which they can be exploited).

3.1. Inorganic Matrices

The principal inorganic matrices listed in Table VII that have been used or proposed to be used as final waste forms for hazardous or mixed wastes are based on cement, gypsum, and sulfur. Among the various types of synthetic cement, portland cement has held a central role, owing to its hydraulic characteristics and widespread use in construction materials [41]. It is similarly a central focus for the purposes of cement-based final waste forms [391]. Gypsum is also an important material for solidification and stabilization applications. It is used as an additive to cement-based systems, and it is the principal component in recently developed proprietary processes [390]. The third principal material that is discussed in this section is sulfur. Although their structural uses were predicted many decades ago, sulfur-based materials have only recently been appropriately developed for commercial use [292,297,309,316]. Current research has indicated that sulfur may be used in final waste forms as either the predominant constituent or one of the principal components in a composite matrix [519,523,525]. The principal concepts described in this section for inorganic matrices are summarized in Table VIII.

3.1.1. Cement-Based Materials

Portland cement is the most ubiquitous inorganic matrix for solidification and stabilization. It and its common variants typify the cement-based materials that are used as final waste forms. In general terms, cement is a finely powdered, calcareous material that, when mixed with water, forms a plastic paste that sets, losing its plasticity, and eventually hardens to a rock-like consistency [23,24,27]. The complex chemical reactions between the cement constituents and the added water, collectively considered as hydration and hydrolysis reactions, foster the development of the strength exhibited by cement. During the overall consolidation process, a rigid interlocking matrix of hydration products is established and slowly replaces the water between cement grains. Ultimately, this network binds the composite mass together and thus provides the strength that is characteristic of cement. Portland cement, in particular, is classified as hydraulic because the hardening that develops after setting can occur underwater and its strength does not depend on either drying or reactions with atmospheric carbon dioxide.

Raw Materials or Starting Components. Portland cement is prepared, as Table VIII indicates, by heating a mixture of materials, one of which is mainly composed of calcium carbonate and the other of aluminum silicates, to high temperatures [23,30,40,41,46,151,390]. In the vicinity of 1450°C [24,45], the silica-containing components (e.g., clay and quartz) react to achieve an equilibrium assemblage of phases. This assemblage consists of two anhydrous calcium silicate minerals—tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$) and β -dicalcium silicate ($\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$) — and other components, principally alumina (Al_2O_3) and iron oxide (Fe_2O_3), which exist as tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$) and a ferrite-aluminate solid solution that has the approximate composition $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ [24,41,45]. Occasionally, two additional anhydrous calcium silicates, the polymorphic α -dicalcium silicate ($\alpha\text{-}2\text{CaO}\cdot\text{SiO}_2$) and γ -dicalcium silicate ($\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$), may be present in portland cement [23]. Lastly, free calcia (CaO) and magnesia (MgO) typically form from cement rock or limestone when these materials are used, and although they may persist, these oxides usually convert nearly completely to other compounds [24]. These phases comprise the resulting product, known as clinker, which partially melts and sinters during the subsequent calcination stages [24,45].

Upon the addition of water to the anhydrous cement powder, the cementation process ensues. In the first few hours, a colloidal calcium silicate hydrate gel forms. This gel eventually hardens over a lengthy

period that can extend from a few days and weeks to over many months, or even years, while continuing to react [27]. During this time, the interlacing network of thin, densely packed silicate fibrils grows from the individual cement particles [24,27,28,151]. This fibrillar microstructure imparts a rock-like hardness to the cement. If waste is present, it becomes entrained in the network, in a manner that is similar to that by which inert filler material (i.e., sand and graded aggregates) is entrapped in concrete [27,29].

Common steps to control the kinetics and thermodynamics of the setting process include adding gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to the clinker and grinding the mixture to a fine powder. Gypsum is sparingly soluble, and the sulfate species help to maintain sufficient plasticity in the wet mix so that it can be handled and worked. The enhanced plasticity delays the initial set for 1 to 2 h. The fine powder produced by grinding has a high specific surface area, on the order of 0.3 to $0.4 \text{ m}^2 \text{ g}^{-1}$, that helps to ensure a high reactivity between the cement powder and the water [23,24,43].

Chemistry and Physics of Process. The attempt to elucidate and to understand the diverse chemical reactions that comprise the setting process for various cements, including portland cement, remains an active area of scientific research [22,39,40,45,46]. This status is especially evident when cement is used as a final waste form [383,392,393]. In this attempt, advanced analytical and surface-chemical techniques are useful in the investigation of cement [36,38] and cement-based solidification and stabilization of a variety of wastes [30,391]. Still, irrespective of whether the cement contains waste species, the development of the cement microstructure critically depends on the exothermic reactions between the calcium silicate minerals and the added water, as summarized by the reactions [22,23,26,41,43],

for tricalcium silicate and

for dicalcium silicate, respectively. Here, the terms C, S, and H denote CaO , SiO_2 , and H_2O , respectively; hence, CH denotes Ca(OH)_2 , and the water, H, is the water retained in drying to equilibrium

[23]. The values of parameters m and n depend on the specific compositions in the poorly crystallized C-S-H gel that was identified earlier as a colloidal calcium silicate hydrate gel and whose production is summarized in Reactions (1) and (2). These compositions are, in turn, sensitive to the water-to-solid ratio in the initial mix [23]. This gel, which initially forms on the surfaces of the cement particles, and thereby coats them, eventually grows into thin, densely packed fibrils that radiate from the individual grains of cement [27,30]. As the hydration and hydrolysis reactions proceed, the growing fibrils gradually penetrate the regions that separate adjacent grains and ultimately become interwoven. Within this fibrillar network, the mineral portlandite, $\text{Ca}(\text{OH})_2$, crystallizes from the precipitated CH, and it remains enmeshed as large angular, plate-like crystals [27,30,45]. The development of a complex pore structure accompanies these morphological changes, and a large pore volume is associated with pores less than ~ 5 mm, a size range that may not be detected by mercury porosimetry analysis [47] and that may require reintrusion data [89].

The reactions between the added water and the other minerals present in the cement mix, viz., $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$, can also be summarized by reactions analogous to those in Reactions (1) and (2) [37,39,41,43]. The phases produced from these materials are complex, and their compositions are very sensitive to the initial composition of the cement mix and other process variables, especially the temperature and the partial pressure of steam, if present [23,30,40,41,46]. Consequently, a discussion of these products is beyond the scope of the present review.

Common Variants. The setting and hardening of portland cement can be adjusted by the addition of certain organic and inorganic chemicals [41,390], and the roles of many of them appear to be understood [383,390,392], at least in part. One common example is calcium chloride (~ 2 wt %, based on the cement content), which greatly increases the rate at which the cement develops strength [17,29,30,41]. The use of gypsum, mentioned earlier, also leads to the formation of calcium sulfoaluminate hydrate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 31\text{H}_2\text{O}$), which can crystallize, in the presence of water, into acicular grains of ettringite [$\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3\cdot 26\text{H}_2\text{O}$] [23,30,394]. These needle-like crystals enhance the rheological properties in the early stages of the setting process and, thereby, improve the workability of the cement. Evidently, these needles eventually decompose slightly, yielding alumina gel and a variety of calcium monosulfoaluminate hydrates of plate-like shape (e.g., $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$) [23,41].

In general, additives that either accelerate or retard the establishment of a rigid matrix may be used to control the setting and hardening processes and are known as admixtures. Accelerating admixtures (e.g., salts and derivatives of lignosulfonic and hydroxy acids and derivatives of carbohydrates and glycols) increase the rate at which the cement develops strength during the hardening stage; in view of the facts that the interlocking fibrillar microstructure is responsible for this strength and that these additives may affect the growth of the individual fibrils which ultimately comprise this network, the effectiveness of these additives may be temperature dependent [29]. Often, these chemicals reduce the required quantity of mixing water that is needed for the desired consistency and workability by about 5 to 15 wt % [24,41,43]. These chemicals are known as plasticizers and, owing to their often hydrophobic nature [41], they may be used to entrain air. The most effective plasticizers, namely, the superplasticizers, are typically salts of linear anionic polyelectrolytes (e.g., salts of sulfonated melamine and naphthalene formaldehyde polymers, modified lignosulfonates, and polymers based on acrylic acid [41,42]) that act as dispersants (i.e., deflocculants). Upon adsorption onto cement particulates, these polymers impart a high electrostatic repulsion³ between the cement particulates, which ultimately reduces the barriers to flow and allows a higher concentration of solids in the cement paste.⁴ Simultaneously, many of these admixtures may also help to retard the setting process or to entrain air in the cement; the entrainment of air is often accomplished by the use of surface-active agents, whose molecular classification may be anionic, cationic, or nonionic and whose adsorption at particulate surfaces underpins their role [23,24,29]. Contrasting this effect of the accelerating admixtures to enhance the strength, the use of hydrocarboxylic acids, lignosulfonates, and sugars retards the setting process [25,30,41]. The central role of these additives appears to be adsorption at the surface of growing particles of hydration products, particularly the C-S-H gel [25,41]. The adsorbed species would constitute a barrier to the further adsorption of Ca^{2+} or silicate ions [32,34,35,38] that is needed for further growth of the gel and the ultimate formation of the fibrils whose growth and interactions underpin the setting process, as described earlier. However, the physicochemical behavior of an admixture may not solely be either to accelerate the hardening process or to retard the setting process. Each effect may manifest itself upon inclusion of a single admixture in the processing scheme. Some admixtures accelerate the hardening process, after

³This repulsion can be monitored by measurements of zeta potential and other relevant properties [86,88].

⁴The high anionicity of these polyelectrolytes renders them far more hydrophilic than the typical plasticizers (viz., salts of fatty acids and alkyl- and aryl-sulfonic acids [41]). This state makes the superplasticizers relatively ineffective at entraining air [41], unlike the typical plasticizers that do so readily.

having retarded the earlier setting stage in which the thixotropic rheology and the plasticity imparted by the C-S-H gel are paramount among the properties.

Other additives are also used to improve the final physical and chemical characteristics of portland cement. As examples, fly ash, silica fume, clay, vermiculite, and soluble silicate may be used to modify the physical properties; a variety of proprietary products is also available for this purpose [33,42,43,44,151,390]. Among other physical properties, the compressive strength is one property of cement that can be improved by regulation of the chemical and physical processes described earlier by the addition of particulate admixtures [42]. Regarding additives that improve the chemical properties of cement, the resistance of the cement to corrosion by sulfate species and dilute acids can be increased by the addition of alumina (Al_2O_3) [24,27,390]. However, the long-term strength of these high-alumina cements degrades, rendering them unsuitable for certain structural applications [27].

Properties. Three distinct areas must be considered in order to summarize the relevant properties of cement-based matrices as final waste forms. Two focus on the processing of the fresh paste and the changes in the hardened cement paste. The third area is the microstructure of the final matrix, which is intimately related to the properties of the high-temperature phase equilibria for the various phases.

The properties of the fresh paste depend on its composition and microstructure: that is, the chemical nature and the physical structure of the components and the physicochemical features of the mixture determine, to a great extent, the properties exhibited by the paste. Also, these aspects influence the processing of the paste. For instance, the rheological properties of the fresh cement paste are quite sensitive to the presence of long-range structure within the paste. This sensitivity is especially important with regard to the suspended particulates. In the absence of long-range structure, Newtonian flow behavior may exist, where the viscosity (η) is independent of the shear rate ($\dot{\gamma}$) and is given by the ratio of the shear stress (τ) to the shear rate [86,88]. The effects of changing the shear rate and shear stress are then reversible and are usually accommodated by the paste, and the times for the paste to equilibrate and the flow behavior to reestablish itself depend solely on the viscosity and the transport forces (e.g., the diffusion and convection forces). Under these circumstances, the equilibration of the paste structure is independent of time, and other time-dependent phenomena, such as hysteresis and thixotropy, are not observed. These systems do not exhibit a yield stress (τ_0).

If long-range forces structure the paste, this situation changes [41]. These forces typically lead to a finite and often large yield stress, τ_0 , which the applied shear stress must exceed in order for the paste to flow (i.e., $\tau > \tau_0$). The presence of a long-range structure may also produce a paste with a τ_0 value that depends on the shear rate and is sensitive to the processing history of the paste. In more complicated cases, time-dependent flow behavior may be present too. Hysteresis (i.e., irreversible, γ -dependent flow properties), thixotropy (shear-thinning behavior), and rheopexy (shear-thickening behavior) are the more common manifestations of a long-range structure [41]. Ultimately, these properties can combine to transform the paste to a gelatinous material.

The Newtonian and non-Newtonian rheological properties are primarily established by the particulate nature of the components within the cement paste. Of course, the physical nature of the particulates depends, in turn, on the composition to a great degree. These aspects have been summarized earlier. The formation of the C-S-H gel and the later development of an interlacing network of silicate fibrils characterize the onset of gelation in the paste [24,27]. During this stage, the suspended particulates behave less as individual units and increasingly as a three-dimensional network as these processes progress. Some additives, viz., dispersants and flocculants, can alter the state of dispersion of the particulates, whereas others (e.g., accelerators and retarders) can alter the chemical pathways by which gel forms and by which the subsequent phase changes occur (i.e., crystallographic modifiers) [41]. In turn, the rheological properties and the more macroscopic properties, such as workability, are altered. When waste is present, the chemical and physical nature of the waste-derived species can similarly affect the fresh cement paste. Tailoring of the initial cement composition helps to ensure the emergence of beneficial waste-derived effects and the curtailment or avoidance of detrimental ones.

Once the gel state establishes itself, its composition and microstructure determine the properties that it exhibits and set the stage for the developing microstructure that determines the properties of the final cement-based matrix. The hardened cement paste appears to be a rigid gel with high porosity and internal surface area, and the pores are filled with the dispersion medium [41]. The principal microstructural features of this paste are the residual (unreacted) cement components, the hydration products, such as those given by Reactions (1) and (2), and the capillary pores. Morphologically, the hardened cement paste consists of large distinct grains, on the order of 10 μm and larger, that are set in a cellular mass of smaller particles and pores [47]. Clearly, the microstructure of the paste is

complicated. Water in this stage is capable of evaporating and thus removed from the paste during drying, or it is incapable of evaporating and therefore retained after drying. Furthermore, the state of hydration varies among the types of grains present [47]; hence, complex and irregular particulates coexist in the hardened cement paste.

Many of the microscopic and macroscopic properties that the hardened paste exhibits are set by its microstructure. For example, the rate of drying, the amount of water retained, the degree of shrinkage, and the existence and extent of cracks are consequences, among others, of the interactions between the microstructure and the external conditions to which it is subjected. Chemical additives, impurities, and waste-derived species affect the interplay of these factors.

Finally, the composition and the microstructure of the final matrix similarly determine the chemical and physical properties that it possesses. Chemical durability and mechanical strength are among the more important properties set in this manner. The volumes of cement, water, and air in the final matrix have been extensively studied [41], and empirical relationships have been established in order to describe, for example, the correspondence between the compressive strength and the porosity. The degree of hydration and the water-to-cement ratio are critical parameters in this approach. However, the pore structure, typically interpreted to be the pore size distribution and the nature of the phases that form the pores, influences the strength in complicated ways. Four generic classes of pores have been established [36,41,45]. These are the macrovoids, coarse pores, mesopores, and micropores. Macrovoids are voids that are larger than 1 μm . The other three are in the submicrometer size range, with micropores possibly being in the nanometer size range.

Whereas a detailed discussion of these pores is beyond the scope of the present report, some salient relationships between the porosity and the final properties are noteworthy. The potential for an improved regulation of the final properties is, thereby, made obvious. The macrovoids are remnant defects introduced during the processing of the fresh cement; for example, bubbles entrained during mixing, if not removed, can generate large voids that are macroscopic in scale. Moreover, in view of the fact that the largest defects (pores and inclusions) in a matrix disproportionately contribute to mechanical failure in a material [175,176], macrovoids may limit the strength of the cement matrix. Importantly, the strength may be determined by the largest voids in the microstructure, even though these represent the

minority of pore sizes in the pore size distribution. This phenomenon means that the processing stages of the cement must be carefully executed, in order to avoid the entrainment of bubbles whose remnant defects (macrovoids) ultimately lead to the premature failure in the cement.

The coarse pores generally reflect the state of packing among the initial cement particulates and the initial composition, namely the water-to-cement ratio. The state of dispersion is clearly critical to the packing and the development of coarse pores. Additives, impurities, and waste-derived species can influence this feature very early in the fabrication process.

Unlike the two previously described types of pores (macrovoids and coarse pores), micropores reflect an intrinsic microstructural feature of the C-S-H gel, whose formation is summarized by Reactions (1) and (2) [36,41,45]. The gel, being composed of colloidal particles, contains pores that constitute the limits to which packing occurs in the gel. Correspondingly, the micropores are on the size scale of the particles formed via the hydration, hydrolysis, and precipitation reactions summarized earlier. Being an intrinsic microstructural feature of cement, the microporosity is likely to be sensitive to the same chemical and physical factors that affect the rate of gel formation, including those that affect the stability of the Ca(OH)_2 , which is produced by the same reactions that generate the gel. Consequently, species that adsorb or deposit at the surfaces of the original cement particulates greatly affect the nature of the microporosity. In turn, the drying stage is affected, as well as the transport of material into and out of these pores. Mesopores are pores formed by combinations of the mechanisms just described and by the subdivision of macrovoids and coarse pores brought on by the growth of ettringite and portlandite in those larger pores.

Finally, the susceptibility of the cement matrix to chemical attack from external species and the ability of species from the interior of the cement to diffuse out are also set by the compositional and microstructural features in the final matrix. Importantly, the pore size distribution is also one of the central aspects to which these phenomena are sensitive [393]. Other factors include the external and the internal pH and the speciation of metal species, particularly that of the polyvalent metals. They are among those that determine the magnitude of the driving forces that induce the penetration of species from the exterior of the cement to the interior, the dissolution of matrix components, and the leaching of species out from the interior.

3.1.2. Gypsum-Based Materials

Solidification processes based on the use of gypsum were developed for nuclear waste applications [385] and are summarized in Table VIII. However, their use appears not to have been extended to hazardous wastes until very recently [390]. Many of these processes are proprietary, especially the details regarding the use of polymer additives [493]. According to Conner [385] and a recent IAEA publication [390], the reports by Rosenstiel and coworkers [493,494] provide details on the Envirostone® process developed by U.S. Gypsum. Other processes that use gypsum are also described in the patent literature [487,488,489, 490,491,492]. These are also summarized in Table VIII. The proprietary nature of the systems described in these reports seems to have limited the investigation and development of gypsum-based solidification techniques: that is, virtually no information is available from independent studies. Consequently, the use of gypsum-based processes for purposes of solidification must be considered to be at the laboratory scale [385]. In view of the fact that many of the claims in the patent literature are unsubstantiated by other reports, these claims are often deemed tentative at best.

Raw Materials or Starting Components. Gypsum, that is, calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and a proprietary polymer [493], apparently a water-dispersible melamine-formaldehyde resin [390], or other organic additives [487,488,489,490,491,492] constitute the core of these materials. The resin is hydrophobic when cured [390], a situation that ensures an increased resistance to water.⁵ Lastly, slag can also be an important inorganic additive [488,489,490,491].

Chemistry and Physics of Process. Although gypsum is an important construction and industrial material [142], the details of its chemistry appear not to be adequately understood for the current purposes. Calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), also known as plaster of paris, is certainly a common material, being easily derived from gypsum by mild heat treatment [141]. The microstructure of this material consists of individual crystals in the form of fine needles [141], making the resultant structure a felt-like arrangement with very fine pores [54]. These crystalline needles of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ interlock and, thereby, provide strength to the matrix. A similar microstructure can be anticipated for the gypsum-based matrices that have been proposed for the purposes of solidification. Additionally, the

⁵Related resins are described later; see Sect. 3.2.1.

microstructures of other low hydrates, viz., calcium sulfate monohydrate ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$), and anhydrous calcium sulfate (CaSO_4), also known as anhydrite, have been extensively studied because they are industrially significant. Hence, in the absence of data to the contrary, these phases may also be assumed to exist in the gypsum-based matrices that are destined for waste applications. Lastly, the crystallographic change from the monoclinic phase to the orthorhombic phase, which accompanies the transformation of gypsum to anhydrite [141], can be expected to affect the ultimate microstructure in complex waste forms that contain calcium sulfate.

Chemical additives can be used to control the setting and hardening processes for gypsum-based materials [142]. As is the situation for cement, some of these additives can be used to accelerate or to retard the development of the solid matrix, but such an adjustment may degrade the ultimate strength of the final matrix. Unfortunately for the present purposes, these additives are often formulated and manufactured by gypsum producers for their proprietary use [142] and remain unknown to the author. Still, it is clear that salts, such as potassium sulfate, can be used to accelerate the setting process. Interestingly, raw (i.e., uncalcined) gypsum itself can also be used for such regulation. As stated earlier, few investigations have been documented regarding the various processes that contribute to the overall setting and hardening of gypsum-based solids. The majority of chemical additives that effectively retard the setting process are organic compounds. Their formulations tend to be proprietary and, consequently, their identification is not apparent. However, a reasonable assumption is that these chemicals have roles in gypsum-based systems that resemble those described earlier for the retarding agents for cement-based matrices.

Common Variants. Selected solids may be useful additives to gypsum-based matrices [142]. Sand, expanded perlite [143], and exfoliated vermiculite [144,145] aggregates are examples. The specific roles of these solids are unclear, owing to the paucity of reliable data on such compositions. Still, the interfacial hydration and the surface charge properties of these additives may be central to their effectiveness in adjusting the setting process in gypsum-based systems. An especially great influence of these properties can be anticipated for systems that contain vermiculite [81,85,145], whose approximate chemical formula is $(\text{Mg,Fe,Al})_3(\text{Al,Si})_4\text{O}_{10}(\text{OH})_2$ and which consists of trioctahedral mica sheets that are separated by double water layers [145,349]. When vermiculite is present, its tendency toward isomorphic substitution and its potential for hydration-related interlayer expansion or contraction

can govern the local particulate arrangement in the matrix. Also, hydration-related morphological changes may affect the thermodynamics and the kinetics of the phase transformations that comprise the late stages of matrix development.

Lastly, in view of the fact that the processing time is relatively short, retarding agents can be used to extend it [390]. Examples include sucrose, calcium citrate, and calcium lignosulfonate [41].

Properties. In view of the fact that these systems are generally proprietary, the link between microstructure and properties is not well documented. Nonetheless, some correlations have already been cited. These pertain to the relationships between the chemistry of the system and the processing of the gypsum-based matrices and between these and the final properties. Whereas the implications of the felt-like arrangement of pores, the interlocking of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ needles, and the resistance to water when hydrophobic polymer resin is used to prepare these systems have not been described in detail in the literature, they are clearly relevant to the establishment of the final microstructure. Extending this concept, the microstructural and compositional features that affect the final properties of this type of matrix need to be clarified by further studies if the proper role of gypsum-based waste forms is to be better anticipated.

3.1.3. Sulfur-Polymer Cement

Sulfur-polymer cement primarily consists of sulfur. It contains low concentrations of organic additives, typically totaling about 5 wt %. The use of sulfur as a base material for purposes of solidification is a recent development. It is predicated upon the progress made in formulating construction materials that are composed predominantly of sulfur. A related structural material, sulfur concrete, resembles sulfur-polymer cement. Its composition differs from sulfur-polymer cement by containing concrete aggregate whose concentration may comprise 63 wt % of the total aggregate-sulfur-polymer cement [305,315]. Although the sulfur may contribute to the matrix properties in this type of concrete, it apparently acts to bind the particulates of aggregate [297,315]. Each type of sulfur-containing matrix is summarized in Table VIII.

The use of such materials was anticipated as early as the 1920s [284,285], but they were only recently considered to be practical [291,292,297,309,311,312]. This transition toward acceptance depended, in part, on the identification of suitable sources for sulfur [297,306,308,316] and the combined technical accomplishments that endowed a variety of sulfur-based materials with desirable properties. These include thermodynamic stability [290,296,302,304,305]; mechanical durability [291,292,293,309,310,311], including under conditions of extreme freeze-thaw cycles [289,293,315]; and chemical resistance to corrosive environments [293,305,312,316].

Raw Materials or Starting Components. Sulfur-polymer cement is typically composed of approximately 95 wt % sulfur and 5 wt % organic additives [316]. A typical composition suggests that the organic components in the final cement are essentially hydrocarbons [525]. The central feature of the generic approach to producing sulfur-polymer cement is the preparation of sulfur melt that contains the desired chemical and particulate additives. Unsaturated hydrocarbon additives, e.g., dicyclopentadiene and cyclopentadiene [300,305,316] and glycols [304,316], are common chemical additives, whereas concrete aggregate [315] and mica [304] are solid additives that are used as particulates in typical formulations for sulfur concrete.

Chemistry and Physics of Process. The central features of the melt processing techniques just mentioned relate to the chemical and physical properties of elemental sulfur. The atomic structure of the sulfur molecules is of paramount importance for the pertinent properties discussed herein. Consequently, the chemical bonding in solid sulfur and the microstructure that it engenders in crystalline sulfur underpin the relationships among composition, processing, microstructure, and properties of sulfur-polymer cement and sulfur concrete. In particular, all crystalline sulfur consists of either rings of sulfur that have from 6 to 20 atoms (S_{6-20}), a series whose end members are cyclohexasulfur (S_6) and cycloicosasulfur (S_{20}), or unbranched chains of sulfur, known as catenasulfur (S_n) [286,295,297,298,303]. The cyclic and chain molecules of sulfur have from 2 to over 10^5 atoms, and, therefore, the molecular weight distribution and its corresponding distribution of molecular configurations depend sensitively on the external conditions [298].

Solid sulfur is allotropic, exhibiting numerous crystallographic forms [286,295,297]. The major allotrope in the sulfur that is melted during the production of the sulfur-based cement and concrete is

cyclooctasulfur molecules (S_8). It consists of three crystallographic forms—viz., orthorhombic sulfur (S_α), which has a melting point of 112.8°C ; monoclinic sulfur (S_β), which has a melting point of 119°C ; and a second, less common monoclinic sulfur (S_γ), which has a melting point of 106.8°C [287,295,297,303]. Upon melting, S_8 gives a yellow, transparent liquid. With further heating, it becomes brown and increasingly viscous above approximately 160°C ; the viscosity attains a maximum value in the vicinity of 200°C and falls at higher temperatures until the boiling point is reached at 444.6°C [287,303]. The changes in color and viscosity reflect the temperature-dependent changes in the ring structure and the degree of polymerization that occur in the liquid state [287,295,297]. Regarding these effects, it is noteworthy that the equilibrium vapor pressure of solid sulfur increases by approximately 900% over the temperature range, 80 to 107°C , as the melting point is approached [297]. Such a change, when considered along with the apparent allotropic transition from orthorhombic to monoclinic near the melting point [287,295,297], suggests that the melting and quenching processes associated with the processing of sulfur may be rather sensitive to the presence of additive, impurities, and waste species.

Common Variants. The melt processing techniques just described can be tailored in many cases to render desirable properties to sulfur-polymer cement and sulfur concrete. Often, this processing involves, at least in part, the selection of suitable additives to the sulfur melt, whether or not the particulates that would be in high concentration, say in sulfur concrete, are already present [297]. Of the many forms of sulfur that can exist at room temperature, only three seem to be of practical interest, viz., orthorhombic, polymeric, and monoclinic [295]. The first is the most stable form. However, polymeric sulfur is obtained by quenching the hot liquid sulfur melt, and the monoclinic form is the stable form near the melting point [297].

The plasticity of freshly quenched sulfur appears to be sensitive to the presence of additives. Low concentrations of organic additives with low molecular weight, e.g., cyclopentadiene and dicyclopentadiene, modify the molecularity and the microstructure of solidified sulfur [300]. The fact that low concentrations of these additives can exert significant effects on physical properties such as rheology—which depends, in turn, on the molecularity of the sulfur—is appreciated. Still, the concentrations at which these additives are often used can be misleading when they are based on weight; a low-weight-percent additive may represent, in fact, a relatively high mole fraction because the molecular weight of sulfur rings is typically low. Hence, these *-diene* additives, upon reaction with

sulfur, may comprise a significant fraction of the number of the individual units in polymeric sulfur. The degree to which sulfur is cross-linked by the reaction products derived from these additives and the physical properties that depend, in part, on the organic cross-links would be, of course, very sensitive to the relative number of such links within a polymer of sulfur rings. Consequently, the detailed mechanisms by which these manifestations are induced are more complex than is generally acknowledged [297]. Additionally, some metal species when present at low concentrations exhibit the ability to react with sulfur, especially in the melt. These findings suggest that the polymeric composition of sulfur and its microstructure in the sulfur-polymer cement (SPC) waste form may also depend, in part, on the composition of waste that is incorporated into the matrix.

Properties. The properties of sulfur in the solid and liquid states establish, to a very great extent, the properties of sulfur-polymer cement. The density of solid sulfur varies from less than 2.0 to greater than 2.2 kg m⁻³, depending on the crystallographic phases present [297,315]. Correspondingly, the melting point sensitively depends on the specific phases, as already mentioned. Other physical properties (viz., tensile and compressive strengths and specific heat) and the chemical properties (e.g., chemical resistance, including attack and solubilization by solvents, oxidation and burning, sublimation transitions, and tendencies to enter into electrochemical and photochemical reactions) are also known to exhibit phase-specific behavior [288,289].

Certainly, this set of dependencies on the crystallographic nature of solid sulfur, of which at least 12 different forms can exist at room temperature [286], reflects a broad range of atomic and molecular arrangements that can exist or coexist. These arrangements are, of course, closely linked to the method by which the solid sulfur forms. The earlier discussions in this section addressed the complex molecularity that can exist, depending on the conditions of temperature and pressure. Although the polymeric nature of liquid sulfur has been stressed in these discussions, the microstructure and the properties of the solids formed from the liquid phase and the effect of polymeric units in the solid have not been expressly addressed. Solid sulfur formed by the rapid quenching of molten sulfur exhibits a higher tensile strength than does the typically cast sulfur, for which the cooling rate is slow [297]. The strength of the quenched sulfur may be more than three times that of the slowly cooled solid. This difference has been attributed to the existence of polymeric chains in the rapidly quenched specimens [297].

A similar situation occurs when the sulfur is chemically modified, as was described earlier [290]. Here, the modifiers may perform any of several functions that affect the final microstructure and, hence, the final properties of the solid [316]. For instance, the cross-linking of the sulfur, accomplished by the reaction of sulfur and olefinic (unsaturated) organic monomers (e.g., limonene, $C_{10}H_{16}$, which contains two C=C sites), retards the crystallization of sulfur and increases the plasticity of sulfur [290,300]. These changes are realized because the polymeric microstructure of sulfur establishes a situation that prevents atomic mobility and crystallization; the magnitude of this effect depends, of course, on the relative concentration of the olefin. This behavior is also sensitive to the molecular architecture of the olefin. The increased plasticity of sulfur reflects the amorphous nature in much of the solid sulfur produced in this manner: that is, the material can be deformed, at least on a microscopic scale [175,176]. This phenomenon requires energy, and, consequently, the area-normalized load (i.e., stress) required to fracture the modified sulfur is greater than that required for the unmodified sulfur. The ability to transform sulfur into a material that deforms plastically stems from the ability to tailor the microstructure. As just indicated, this type of transformation can be induced, in the case of sulfur, either by adjusting the physical conditions during processing, as in the case for the quenched sulfur, or chemically, as in the case of the cross-linked sulfur. In practice, the proper regulation of the processing conditions demands that both approaches be used [290,297,316]. Modifications of the microstructure, brought about via the inclusion of nonreactive solid phases (e.g., aggregates and fibers), are also used to enhance the mechanical properties of sulfur [289].

Many of the benefits of this approach, that is, the exploitation of the microstructural changes in order to instill desirable physical and chemical properties in the final product, have been recognized for sulfur concretes and sulfur cements [291,292,297,302,304,305,311, 314,315,316]. Reasonably, this approach has been adapted to the development of waste forms based on sulfur [519]. The chemical resistance in these cases (viz., resistance to corrosion by strong acids) has also been linked to the microstructure of the final sulfur-based materials, as well as to their composition [519].

3.2. Organic Matrices

The principal organic matrices listed in Table VII that have been used or are proposed to be used as final waste forms for hazardous or mixed wastes are thermosetting resins and thermoplastic polymers. The

principal organic matrices for solidification and stabilization applications are summarized in Tables IX and X. The thermosetting resins that are leading candidates for the pertinent applications considered herein are based on urea-formaldehyde copolymer resins; polyether materials, of which the epoxy-based resins⁶ constitute an important family; and polyester polymers [151,385]. The major candidates among the thermoplastic matrices are bitumen, which is composed of a wide variety of mixtures of high-molecular-weight liquid and solid hydrocarbons and vinyl-based materials, such as polyethylene [151,378,385].

Thermosetting resins change irreversibly under the influence of heat, although little or no heat may be required in specific cases. This process involves the generation of a covalently bonded, cross-linked network that is thermally stable. This network changes the initial fusible and soluble material into an infusible and insoluble matrix [187]. The members of this family, irrespective of the specific chemical composition, are hard and brittle (i.e., compared with their non-cross-linked analogues), and they do not melt [179]. Thus, these materials must be cast prior to formation of the network. This requirement demands, in turn, that an understanding of the polymerization reactions and their effects on the viscous and thermal properties of the resin as it undergoes curing [184,201,202] is established. Among the various types of thermosetting resins, matrices based on urea-formaldehyde copolymers occupy a central role because they are the most thoroughly tested for solidification applications [151]. Other pertinent thermosetting polymers for waste disposal are based on epoxy resins and unsaturated polyesters [91,92].

Thermoplastic polymers soften and flow when heat and pressure are applied. These changes are reversible, and the softening and hardening that are respectively induced by increasing and decreasing the temperature, for instance, can be repeated over many cycles [179,187, 224,228]. Thus, the processing of thermoplastic materials generally does not involve major changes in the chemistry of the materials. Provided the viscous and thermal properties of the resin being processed are known, thermoplastic operations can be analyzed and performed in a predictable manner [184]. This flexibility in processing permits the casting or other shape-forming step [185,187,202] to be conducted as deemed best for the overall fabrication scheme. The principal member of this group of potential final-waste-form matrices is asphalt or bitumen. It has been successfully used to dispose of radioactive waste [385]. Another

⁶The term *epoxy* reflects the starting material, epichlorohydrin, and the presence of the epoxide groups in the polymer prior to the cross-linking process [187].

important thermoplastic is polyethylene, which is the simplest member of this polymer family and is extensively used industrially and for consumer applications [224]. Lastly, some thermoplastic polymers can also exist in thermosetting configurations; for example, the polyester resins offer this flexibility [224].

3.2.1. Thermosetting Resins: Urea-Formaldehyde and Related Condensation Resins

Raw Materials or Starting Components. The raw materials for urea-formaldehyde (UF) resins are, of course, urea and formaldehyde, whose chemical formulas may be depicted as

(I)⁷

and

(II)

respectively.⁸ Each is difunctional, meaning that the urea and formaldehyde molecules have, respectively, two reactive amide groups, $-\text{C(O)NH}_2$, and two aldehyde groups, $-\text{C(O)H}$. The monomers are copolymerized, predominantly via condensation processes. The final product is polymeric, with composition whose repeat unit may be represented by the following formula [188]:

(III)⁹

⁷The scheme used herein to identify compounds consists of parenthetical roman numerals.

⁸The symbol C(O) is used herein to designate carbonyl groups. A double covalent bond exists between the carbon and oxygen atoms. Thus, the bonding denoted by C(O) is $>\text{C}=\text{O}$.

⁹The symbol ~, which appears in the formula as $\text{CH}_2\sim$, designates that a variety of condensation pathways is available and that these would generate different chemical linkages to the core of the repeat unit.

Urea is the principal amine-containing reagent used to prepare amino resins, but many others can suitably copolymerize with formaldehyde to yield resins that are similar to the UF resins [187,196]. Melamine, thiourea, guanidine, cyanamide, and dicyanodiamide are commonly used for this purpose, and acid amides, guanamines, aniline, and substituted ureas are used to a lesser extent [196]. Similarly, whereas formaldehyde is the most important carbonyl-containing reagent used industrially to make these resins, others (notably, furfural and glyoxal [196]) can be used to make amino resins with similar compositions. The prevalence of the two monomers, (I) and (II), in the production of UF resins is linked to their relatively low cost [225]. Still, their physical properties are often inferior to those of related amino resins [196,231].

Other materials may include various modifiers, whose role is to effect important changes in the properties (e.g., tensile strength and hardness [187]). Usually, these chemicals are added in small amounts. Typical modifiers are alcohols, amines, aminoalcohols, and various inorganic substances [196,231].

Dispersions of partially polymerized UF resins, often described as urea-formaldehyde precondensates [196], may be used [385,496]. They are typically prepared via emulsion polymerization [188] and can be mixed in desirable proportions with water, including that which contains hazardous or mixed waste, and an acidic curing agent in order to complete the polymerization process [385,496]. The gelation and setting of the process are controlled by the curing agent selected and the specific processing conditions chosen, particularly the mode of mixing used.

Chemistry and Physics of Process. The production of UF resins principally consists of two stages [187,196]. The first one is hydroxymethylation (i.e., the generation of $-\text{CH}_2\text{OH}$ groups), in which the amide groups of urea (I) react with formaldehyde (II) to produce an intermediate (IV), such as

The double underlining denotes the remnant from the original urea molecule. In practice, this process is catalyzed, usually in an alkaline medium.

The second stage consists of condensation, and it may be carried out either after the hydroxymethylation or at the same time. An example of the condensation process is provided by the intermediate compound (IV). If one molecule of urea reacts with a terminal hydroxymethyl group (viz., a $-\text{CH}_2\text{OH}$ site) of species (IV), the organic product (V) would be

for which the portion contained within the braces, {}, derives from this second urea molecule. This portion may further react in a manner that resembles the hydroxymethylation step used to obtain species (IV). One molecule of water is also produced in the condensation step. Typically, the condensation process is catalyzed under acidic conditions [231]. Then, it is possible to regenerate formaldehyde (II) if two hydroxymethyl groups reside on neighboring intermediates. However, both water and formaldehyde are produced in this process [187,196].

Further condensation steps that involve species such as those described thus far lead to longer chains. Ultimately, a polymeric UF resin, such as species (III), is produced. Within this repeat unit, the fundamental linkage that characterizes UF resins is the sequence $-\text{N}-\text{C(O)}-\text{N}-\text{CH}_2-$. Incomplete condensation may permit segments of the polymer to retain the remnants of the hydroxymethylated species (IV); then, the localized repeat unit may resemble the polymeric unit,

more than the ideal structure with repeat unit (III). Sometimes, the prevalence of the hydroxymethyl (i.e., $-\text{CH}_2\text{OH}$) groups is reduced by partial esterification reactions [196].¹⁰ The hydroxymethyl groups along the backbone of species (VI) are sites for later cross-linking that produces a three-dimensional network.

¹⁰Esterification reactions, especially those that involve condensation processes, are described in Sect. 3.2.3.

The production of UF resins, prior to the cross-linking stages, may be batchwise, continuous, or a combination of the two [187,196]. Batchwise procedures constitute the most commonly used approach. They typically permit an extensive variety of products to be made and are amenable to frequent changes in procedure. However, production capacity is relatively small. As stated earlier, the hydroxymethylation and condensation reactions are often sequentially conducted. These are carried out in aqueous media. Upon completion of the condensation stages, the water that is produced and the water used to introduce the reagents are evaporated under a reduced pressure. The production of UF resin powders is accomplished by first producing the aqueous resin solution, followed by a spray drying step during which the solution is atomized and the water from the droplets subsequently evaporates. The powder is then collected.

Continuous processing is used in situations that demand a very uniform quality of product [187,196]. However, the range of products must be relatively narrow, even in these cases. The throughput of a continuous operation must be strictly maintained, and changing the product is not simple. Manufacturing operations may consist of a complicated arrangement that involves batchwise processing at certain stages and continuous processing at others [196].

Irrespective of the processing mode, a large number of processing parameters affect the end product and its properties. These include, among others [187,196,231], the purity of the starting materials, the concentrations of these reactants, the molar ratio of derivatives of the urea and formaldehyde monomers in each reaction stage, the pH value at each stage of the operation, the temperature of each stage, the type and amount of catalyst, and the reaction and residence times in each stage. Monomolecular and hydroxymethyl compounds, such as compound (IV) and oligomers that resemble polymer (VI) but which have low degrees of polymerization (say, those with n values of 6 or less), can be prepared in pure form [196]. Despite the fact that aqueous solutions of these oligomeric materials are unstable, the solid forms of these products are stable for extended periods of time [196], and, therefore, may be substituted as starting materials in lieu of urea and formaldehyde.

Common Variants. One variant group on the systems just described is the family of polyurethanes [187,195,210]. Members of this family are produced via the condensation of a urethane (i.e., a carbamate),

with an aldehyde [196]. The fundamental group in the polyurethanes produced from this type of reaction is $-\text{NH}-\text{C}(\text{O})-\text{O}-$ [187]. During the reaction sequence, which is initiated under basic conditions, the urethane (e.g., ethyl carbamate, where C_2H_5- is the R-group) reacts with the aldehyde—such as formaldehyde, compound (II)—to yield hydroxymethyl compounds, which resemble intermediates (IV) and (V). The reaction proceeds in a manner analogous to that described earlier for the UF-repeat unit (III) and the polymer (VI). When the conditions are changed to acidic, the hydroxymethyl compounds cross-link and form bridges that lead to thermosetting polyurethane resins [187,196,210]. Various alternatives exist to the starting reagents mentioned here [187,196,213,220,222]. Typically, the cross-linking stage consists of the formation of urea-like linkages [187]. Then, some of the intermediate steps in the polymerization may be summarized, according to Reactions (3) and (4).

Compound (VIII) is an alkylisocyanate. The hydrolysis reaction in Reaction (3) demonstrates that, as this compound is converted to an alkyl amine (IX), carbon dioxide is generated. A second alkylisocyanate, compound (X), which may differ from compound (VIII), reacts with the alkyl amine, according to Reaction (4). The product, compound (XI), contains a urea-like link, which is denoted by the double underlining in Reaction (4); comparison of the structures for urea (I) and product (XI) reveals the similarity.

Different sets of alkyl derivatives can be selected. Hence, the properties of the resulting polyurethane resins vary as the nature of the alkyl groups changes. Various hydroxy-containing reagents may be used

¹¹The prime (') indicates that the alkyl group may differ from the one in compound (VIII).

either in lieu of or in combination with those already described [187,196,195,210,213]. Moreover, the mixture in which the polymerization occurs is complex. If a diisocyanate, that is, a member of the family whose representative formula is

is used, the reaction summarized in Reaction (4) may occur between oligomeric or polymeric fragments [187]. This type of compound is typically used, in combination with glycols, to produce polyurethane resins. Rigid polyurethane foam is the thermosetting resin network that results when these reactions are carried out in the presence of catalysts that promote the production of foam by stabilizing CO₂ bubbles produced via the hydrolysis in Reaction (3); these catalysts are amine-derived surfactants or stannous-ion-containing soaps [187,214].

Mixed resins that are based on urethane [e.g., a monoisocyanate or diisocyanates such as compounds (VIII) and (XII), respectively], urea (I), and formaldehyde (II) can also be made [187]. The properties of these resins make them suitable for surface coatings. Although the copolymer resins that have been made for use as coatings are not particularly germane to final waste forms per se,¹² their existence suggests that urethane copolymers may be useful if the comonomer is suitably selected. This approach has been pursued. As an example, many copolymers made with urethane and unsaturated monomers (i.e., the vinyl compounds discussed in Sect. 3.2.3) are possible [183,189,211,216, 244,246,247,248, 249,250] and have been known for many years. Often, the processing of the copolymer resin can be improved [189,201], or the properties of the final resin can be tailored [246,248,249]. Still, the ultimate copolymer properties depend on the intimate relationships among the chemical composition, the processing history, and the microstructure during fabrication processes [187,188,204,221,225,231]. The physical microstructure and morphology can be assessed using various microscopic techniques [206,207,219,224] and, possibly, by advanced and interdisciplinary analytical and small-angle-scattering approaches [203,229].

¹²Coatings having tailored properties may be useful, however, if membranes of controllable transport properties are found to be useful in waste disposal applications.

A potential limitation for the uses of polyurethane as final-waste-form matrix is the fact that toluene diisocyanate, which is a commonly used reagent in the production of polyurethane foam, is itself regulated under RCRA [233]. However, recycling efforts and improvements in process design appear to be promising approaches to reduce the hazardous waste streams generated in the production of polyurethane foam [234].

Properties. The properties of thermosetting resins can be subdivided into two groups, namely, those that relate to the general families of polymers and those that describe the individual polymers. Examples of the first set of properties focus on the influences that the cross-linked or network microstructure have on the processing of these materials and on their general behavior. Specifically, the network structure is rigid, and it does not soften and flow at elevated temperatures. Two important consequences of this behavior are stressed here. The first affects the processing, and the other establishes the final mechanical properties.

Regarding the processing of thermosetting resins, the curing stages (i.e., polymerization to establish the network) in the processing scheme must be postponed until the component has been shaped. Similarly, the polymer cannot be remelted after curing because the network is irreversibly formed, as described earlier in this section. These processing requirements mean that molding techniques, such as compression molding, are needed. In this method, a mold is filled, and heat and pressure are applied. Typical conditions of temperature and pressure are 150°C and 7–21 MPa, respectively [187]. Still, the thermal and rheological properties of the materials prior to complete curing may demand considerably different conditions.

Regarding the mechanical manifestations of the inability of thermosetting resins to soften and to flow at elevated temperatures, the tensile strength and hardness are particularly noteworthy. The network structure ensures a high strength and hardness because multiple bonds must be deformed and then broken in order for these materials to fracture. However, the network also has an inability to deform plastically. Hence, it exhibits brittle fracture characteristics [175,176]. In order to reduce the brittleness of such materials, additives, usually solid fillers, are needed. An example of this requirement is provided by the use of sawdust in phenol-formaldehyde resins (i.e., Bakelite) [175]. Similarly, the network underpins the dimensional stability that these polymers exhibit.

The network microstructure also helps to ensure good resistance against chemical attack and thermal degradation below the decomposition temperature. Low flammability and low absorption of moisture are also related to the network microstructure [187]. Unfortunately, the low permeability of moisture may act in reverse to increase the amount of water retained in thermosetting resins used as final waste forms. Retention of the acidic water produced upon polymerization has been observed for UF resins with undesirable effects for waste disposal [385].

3.2.2. Thermosetting Resins: Epoxy-Based Polyethers

Raw Materials or Starting Components. Another condensation process that is used to obtain useful resins focuses on the polymerization of epoxy monomers. These monomers possess a three-membered cyclic ether group [187,190,242],

and they are often compounds of the type,

for which the R- and R'-groups may be identical or may differ [187,204]. If these groups contain sites that can enter into condensation reactions with the epoxide ring once it is opened, polymeric structures can be made. Moreover, if the R- and R'-groups contain chemical moieties that have limited ability to twist and to alter its local conformation, as is often the case with phenolic groups (i.e., groups with a benzene-like ring, C₆H₅-), rigid polymer resins result [204]. Sometimes, epoxy monomers are copolymerized with difunctional compounds in order to tailor the polymeric chain in rigid resins. Consequently, such materials are often made, as described next, with bisphenol A, a diol, and epichlorohydrin, the epoxy monomer.

Chemistry and Physics of Process. Bisphenol A, which has the formula,

where the symbol ϕ represents the phenyl group, and epichlorohydrin, whose formula is

are commonly used to prepare epoxy resins [204]. The resins have the generic formula

and exhibit a range of useful properties, including toughness and rigidity. The ether linkages (viz., the $-\phi-\text{O}-\text{C}-$ functionalities), two of which are in the repeat unit in polymer (XVII), provide chemical resistance [190]. The terminal groups in oligomers, for which the value of n is in the interval 1 to 4, have the structure displayed by species (XIII) and are capable of further reaction. Together with the hydroxyl groups ($-\text{OH}$), they generate the adhesive properties that are commonly associated with epoxy resins [190,242]. These two types of groups can also enter into cross-linking reactions and, thereby, impart the thermosetting properties [208]. Inorganic fillers can be used to improve the resistance to abrasion, though the tensile and flexural strengths generally degrade when this is done [204].

Epoxy resins are used in combination with polyfunctional coreactants or curing agents. Their multiple reaction sites permit them to act as cross-linking agents [187,190,204,208,242]. Polyamines, polyamides, polyphenols, polycarboxylic acids, and anhydrides are common examples.

Common Variants. Many of the curing agents just cited exhibit detrimental toxicological effects. This problem is especially acute with aromatic diamines. Therefore, efforts to find alternative curing agents

for epoxy resins are ongoing. Polycycloaliphatic polyamines, however, offer improved processing and reduced toxicological hazard [240]. Curing is rapid with these saturated polyamines, and the epoxy resins cured with such agents exhibit excellent mechanical properties.

Properties. The properties that derive from a network structure were described earlier; see Sect. 3.2.1. Cross-linked polyethers that are based on epoxide reactions exhibit similar microstructure-property relationships.

The broad range of potential coreactants for the synthesis of epoxy-base polyethers and the fact that the final properties are partly determined by the coreactant lead to a broad spectrum of potentially available properties. Inversely, the selection of the coreactant is greatly influenced by the performance criteria that must ultimately be met. One example builds upon the earlier discussion regarding the lack of ability for the polymer chain to flex, to twist, and to reorient itself, owing to relative rigidity in the bonding along the backbone or steric hindrance of the side groups. This is the set of phenyl-containing coreactants. They are selected when good mechanical properties are desired. Polymers prepared with these types of agents also tend to exhibit superior resistance to elevated temperatures [208].

3.2.3. Thermosetting Resins: Unsaturated Polyesters

Raw Materials or Starting Components. One set of raw materials for unsaturated polyester polymers consists of diols and dicarboxylic acids with the general formulas

and

respectively, where the species R and R' denote aliphatic or olefinic entities [188].¹³ The aliphatic derivatives consist of saturated hydrocarbon chains with the formula C_nH_{2n} , whereas olefinic derivatives contain unsaturated bonds (viz., $C=C$), such that the formula for the hydrocarbon portions in R and R' is C_nH_{2n-2} . At least one of the monomers, namely, the diol (XVIII) or the dicarboxylic acid (XIX), must possess at least one unsaturated bond that would permit the cross-linking of polymeric chains and the subsequent establishment of the network structure that is central to thermosetting resins.

Chemistry and Physics of Process. The dissimilar alcohol ($-OH$) and carboxylic acid [$-C(O)OH$] groups in compounds (XVIII) and (XIX) react, via a condensation process, to form ester linkages. This reaction is called esterification. These generic compounds, monomers (XVIII) and (XIX), thereby lead to polymers with the general formula

Here, the double underlining emphasizes the ester group and the olefinic entities that it links. A by-product of the condensation reaction between a diol and an dicarboxylic acid is water [188].

A second type of reaction is used in order to cross-link the growing polyester chains. This reaction involves the unsaturated site in R or R' and is an addition reaction. Addition reactions underpin much of the industrial production of plastics [187,209,212,218,235]. Unsaturated monomers, such as the vinyl compounds which have the generic formula,

where X represents any of a variety of chemical functionalities, are typical reagents for this class of reactions. Vinyl monomers with X-functionalities of phenyl (C_6H_5-), halogen (Cl- and Br-), methacrylate

¹³The prime (') indicates that the diol and dicarboxylic acid may contain different aliphatic entities.

[CH₂C(CH₃)C(O)O-], and cyano (N≡C-) groups are used to make, respectively, polystyrene, poly(vinyl chloride) (when Cl is the halogen), poly(vinyl methacrylate), and polyacrylonitrile, respectively [182,187,188,228,235].

Styrene, which has the formula

where ϕ denotes the phenyl group, is typically used as a cross-linking agent for the polyesters considered here [187]. The pathways by which it homopolymerizes and reacts with the unsaturated sites in R and R' differ significantly from those discussed earlier for the resins made by condensation routes. Whereas condensation polymerization proceeds by stepwise intermolecular reactions to yield water or hydrochloric acid as by-products, as described for UF resins (Sect. 3.2.1), addition polymerization mainly proceeds by a chain mechanism that involves the generation and reactivity of especially active centers of one sort or another [182]. One type of active center is the free radical, an example of which is the vinyl-derived species,

where the free radical is denoted in the formula by the raised dot [182,188] and the symbol, $\sim$, suggests the general nature of the original vinyl site: that is, this schematic of the free radical species (XXIII) applies whether the original site resided within a larger molecular architecture, such as in R and R' in compounds (XVIII) and (XIX), or was in styrene (XXII). Being very reactive, these species can combine with one another to form oligomeric and polymeric chains. Using styrene as an example, addition polymerization would produce macromolecular polystyrene chains of the type

In the present context, polystyrene cross-links would be characterized by low n values. These links would then form between similar R- or R'-groups on neighboring chains, if only one type of the original monomers, that is, either the diol (XVIII) or the dicarboxylic acid (XIX), was unsaturated. Of course, R- and R'-groups on separate chains could be linked via polystyrene bridges if both types of monomers were unsaturated. These addition polymerizations that establish the cross-links do not lead to the types of by-products, such as water, that are produced in condensation reactions.

Common Variants. Other chemical reactions can be used to generate unsaturated polyester polymers [187,188,213,218,220,222,228]. Among those that are condensation reactions, the esterification of a hydroxycarboxylic acid having the generic formula,

resembles the reaction between diol (XVIII) and dicarboxylic acid (XIX) that was just described [182]. Here, the hydroxycarboxylic acid contains the two different chemical functionalities in one molecule, and its polymerization leads to macromolecules of the type

As for the condensation reactions that lead to polyester (XX), the polymerization of hydroxycarboxylic acid monomers to obtain polymer (XXVI) also produces water. The amount of water generated in this case, however, is approximately half that generated when diol and dicarboxylic acid monomers are copolymerized to make polyester (XX).

The cross-linking process described earlier can similarly occur with the polyesters made by the homopolymerization of hydroxycarboxylic acid monomers (XXV). The R-moiety in the difunctional monomer must have an unsaturated site that can react with vinyl-based cross-linking agents (e.g., styrene).

Another condensation reaction that resembles the esterification reactions already mentioned is the esterification of acid chlorides [188]. This reaction is analogous to that described for the production of polyester (XX). However, an acid chloride, in this case a diacid-dichloride,

is reacted with a diol such as that represented by formula (XVIII). Polyester (XX) is again a representative product. The by-product of this polymerization is hydrochloric acid, rather than water.

An altogether different type of variant on the polyester materials described thus far is the family of cross-linked poly(vinyl esters) made via the polymerization of vinyl monomers with the generic formula,

in which the ester link, $-\text{C(O)O}$, resides in the vinyl substituent enclosed in the braces, {}, and the R-group is typically a saturated alkyl group with the formula, $\text{C}_n\text{H}_{2n+1}$ [209,212,235]. Vinyl ester monomers in which the R-groups are a lower alkyl (viz., $n \leq 6$) type are the most common ones.

Comparison of the structures in compounds (XXI) and (XXVIII) indicates, after considering the structure of polystyrene given by formula (XXIV), that the linear poly(vinyl esters) have the generic structure

Poly(vinyl acetate), poly(vinyl propionate), and poly(vinyl pivalate) represent these materials, where the R-groups are CH_3 , C_2H_5 , and $t\text{-C}_4\text{H}_9$, respectively, and the homopolymers and copolymers of vinyl acetate are the most important members of this family. Derivatives of higher alkyls are also used industrially, and poly(vinyl 2-ethylhexanoate) and poly(vinyl laurate) typify these poly(vinyl esters), where the respective R-groups are $-\text{CH}(\text{C}_2\text{H}_5)_5$, $-(\text{CH}_2)_3\text{CH}_3$, and $-(\text{CH}_2)_{10}\text{CH}_3$.

Cross-linking is accomplished by introducing a difunctional vinyl monomer, such as divinyl benzene,

into the monomer system at a relative concentration that is set by the desired cross-linking frequency. Addition reactions at the vinyl sites ensure the cross-linking of otherwise poly(vinyl ester) chains.

Properties. As is the case for the matrices discussed in Sect. 3.2.1, the properties of the thermosetting matrices discussed in this section, namely, those derived from unsaturated polyesters, can be also subdivided into two groups: properties that relate to the polymer families and those that describe the individual types of polymers. Major examples of the first set of properties focus on the cross-linked network microstructure. As stated earlier, the network structure is rigid and does not soften or flow at elevated temperatures. The influences of this property that were described earlier—i.e., that the curing (polymerization to establish the network) stages in the processing scheme must be postponed until the component has been shaped—apply to the cross-linked matrices derived from unsaturated polyesters. Of course, if low cross-linking frequency is acceptable, the linear chains of polyester molecules can be grown to macromolecular sizes, while retaining the remelting properties associated with thermoplastic resins (see the Sects. 3.2.4 and 3.2.5). This approach resembles that taken in vulcanization processes [187]; rubber-like matrices then result.

Returning to the matrices in which the degree of cross-linking is extensive, we can anticipate that thermosetting matrices based on cross-linked unsaturated polyesters will not soften and flow at elevated temperatures. Good mechanical properties, such as those described earlier for network microstructures, can also be anticipated. Again, the reasons lie in the multiple cross-links that are difficult to deform or to break, as would be required in order for these materials to fracture. However, such resistance to deformation can make these thermosets brittle [175,176].

Certainly, the network microstructure helps to ensure resistance against chemical attack and thermal degradation below the decomposition temperature. Low flammability and low absorption of moisture are

also related to the network microstructure [187]. The permeability to moisture may depend on the hydrophobic-hydrophilic balance that characterizes the polyesters.

An important limitation of the poly(vinyl esters) is that alkaline aqueous solutions can degrade the polymers [235]. This attack occurs via saponification of the ester groups [182]. Here, the ester group is hydrolyzed to yield sites that resemble the salts of fatty acids, while the alcohol molecules are concomitantly generated. For instance, consider the simple ester, $R-C(O)-OR'$. Saponification by an alkali base, such as KOH, produces $RC(O)O^-K^+$ and $R'OH$. Whereas the degradation of poly(vinyl esters) via similar processes can be slowed by suitable selection of the R-groups in the monomers, it cannot be eliminated if the polymer contacts alkaline aqueous media.

3.2.4. Thermoplastic Polymers: Bitumen

Raw Materials or Starting Components. The primary source for bitumen is petroleum crude [8,9,10]. The bitumen is contained in a precipitated asphalt by-product of the solvent treatment in which gas oil and lube distillates, which were not previously removed as volatile and distillable fractions from the petroleum crude in the earlier distillation stages, are recovered. Normally, it is separated from the remainder of the precipitated asphalt by solvent extraction. Bitumen may also be obtained, generally mixed with mineral matter, from a native (natural) deposit that represents aged and weathered petroleum crude oil which had escaped through the earth's surface layers long ago. This bitumen is commonly referred to as native asphalt. Unless stated otherwise, the ensuing discussions in this report pertain to bitumen derived from petroleum crude or are of a generic nature that applies to bitumen from both sources.

In view of the fact that the composition of bitumen is varied and generally nonspecific, the complex composition is commonly defined by the mass fractions of the major hydrocarbons in the bituminous material extracted. Four generic fractions exist in most bitumens, based on dispersion and precipitation in *n*-heptane, and the relative proportions of these fractions characterize bitumens of different sources and treatments [8,9,10]. These groups are saturates, naphthene aromatics, polar aromatics, and asphaltenes.

The first two fractions largely consist of low-molecular-weight liquids [9]. The saturates comprise pure paraffins, pure naphthenes, and mixed paraffin-naphthenes, and the average molecular weight is 610 g mol^{-1} . The naphthene aromatics consist of mixed paraffin-naphthene aromatics and sulfur derivatives, and the average molecular weight of these is 725 g mol^{-1} . The densities of these two fractions are 0.87 and 0.97 g cm^{-3} , respectively. The corresponding values of viscosity are 0.1 and $2.2 \text{ Pa}\cdot\text{s}$ at 60°C .

The polar aromatics and asphaltenes consist of high-molecular-weight solids that are viscoelastic at ambient temperatures and viscous at higher temperatures [8,9]. The first group comprises mixed paraffin-naphthene aromatics, whose structures consist of multiple rings, and sulfur, oxygen, and nitrogen derivatives. The average molecular weight of these constituents is 1090 g mol^{-1} . The asphaltenes are solids of mixed paraffin-naphthene aromatics, whose molecular architecture contains polycyclic structures, and sulfur, oxygen, and nitrogen derivatives but is not set by a stoichiometric formula [5,6,9]. The average molecular weight of this fraction is 5300 g mol^{-1} . The densities of the polar aromatics and the asphaltenes are 1.07 and 1.15 g cm^{-3} , respectively. The viscosity of the first group of solids exceeds $10^5 \text{ Pa}\cdot\text{s}$ at 60°C , whereas that of the asphaltenes is too high to provide a representative value [9].

Approximate ranges for their relative concentrations, based on mass, are 5 to 15% saturates, 30 to 45% naphthalene aromatics, 30 to 45% polar aromatics, and 5 to 20% asphaltenes. Consequently, the average molecular mass exhibits a range of values that depend on the source and the treatments by which the bitumen was derived. A nominal range is 900 to 1100 g mol^{-1} .

Bitumen is a complex colloidal system [1,4,9], and its rheological properties reflect a mixture of properties that are attributable to its sol-gel behavior [2]. In particular, micelles of the larger constituents (viz., the polar aromatic and asphaltene fractions) appear to be dispersed in a medium that mostly comprises the lower-molecular-weight constituents (viz., the saturates and the naphthene fractions) [1]. Organic surface-active additives, similar to those used to stabilize and to control nonaqueous pigment dispersions [82], can be used to tailor some of the colloidal properties of bitumen. The great differences in rheology [2] and relaxation behavior [3] that bitumens can exhibit have been attributed [1,2,9,10] to the different degrees of peptization that exists in these emulsions.

Chemistry and Physics of Process. Three main types of bitumen exist: distilled, air blown, and emulsion bitumens [8,9,10]. The first two of these have been extensively examined for their waste-form capabilities [371,376,377,378].

Distilled bitumen is the type just described. It is the product obtained by the cracking of petroleum crude via distillation and solvent extraction methods [378]. This bitumen is a complicated mixture of complex molecules and, as a result, does not exhibit a well-defined set of molecular properties, such as melting point. Instead, it softens. The transition from the solid phase to the liquid phase occurs over a broad range of temperatures. This range is nominally 38 to 72°C. The hardness of distilled bitumen, as indirectly assessed from measurements of the penetration depth of a needle, under a load of 100 g at 25°C is low; the depth obtained after 5 s, the standardized duration for the test [378], is in the range 10 to 100 mm [9,10,378].

In the air-blowing (oxidizing) process [8,9,10], bitumen is converted to a harder product by contact with air in either a batchwise or continuous operation. This process is conducted in the temperature range 200 to 275°C [10] and is designed to react the oxygen in the air with the hydrogen in the bitumen. This oxidation of bitumen produces water vapor and generates unsaturated sites in the molecular structure that can be subsequently used to cross-link the material. It also increases the asphaltene content, leading to more strongly associating compounds without an increase in the molecular weight [7,9]. This conversion process is affected by many processing variables. The composition of the bitumen, its consistency, the temperature, the flow rate of air, and the presence of catalysts are among the major ones [9].

Although this description suffices to summarize the fundamental chemistry and underpins the design of the air-blowing process, the situation appears to be considerably more complex [10]. Constituent species that contain higher concentrations of nitrogen, oxygen, and sulfur, which are the more polar constituents, appear to react preferentially with the oxygen in air. As a result of the increased relative concentrations of asphaltenes that are insoluble in hexane, which accompanies this phenomenon, the dispersed state of the oil-in-water emulsion described earlier is degraded [10].

Thus, the microstructure of the bitumen is altered as the material is converted by contact with air into a harder, less plastic substance. The chemical changes that are central to this conversion are accompanied

by changes in the physical arrangements within the complicated bitumen mixture. Together, these two sets of changes alter the physicochemical properties that are detected macroscopically. The softening point of this bitumen lies within the temperature range 80 to 90°C, and, on average, the hardness of air-blown (oxidized) bitumen, as determined via the procedure described for distilled bitumen, exceeds that for distilled bitumens and covers a narrower range than that spanned by the distilled bitumens. The penetration depth, measured via standard procedures, typically lies in the range 35 to 45 mm [378]; the analogous range for distilled bitumen cited earlier is 10 to 100 mm. Consequently, oxidized bitumen is less deformable than its distilled (unoxidized) counterpart.

Emulsified bitumen is a dispersion of the bitumen in water that is prepared by any of a diverse set of procedures [9]. An emulsifying agent is used to accomplish this dispersion [80,84]. Cationic surfactants (long-chain organic amines) and anionic surfactants (e.g., salts of fatty acids) are used as emulsifying agents. The droplet size is on the order of 5 μm . Nonionic derivatives of cellulose can be used to increase the viscosity of the emulsion to desired values. Rapid-, medium-, and slow-setting emulsions can be made, and the rate of the setting process is tailored for the application [9,10].

Common Variants. The processing of bitumen offers many opportunities to modify its composition, and various materials may be added to it in order to modify its properties [9,10]. Many of the variants are outside the scope of the present report. Still, it is noteworthy that the use of fillers and fibers to reinforce bitumen and the use of sulfur to bind and to harden bitumen¹⁴ are two examples that relate directly to the microstructure of bitumen and the effect of this microstructure on the properties of the material. Moreover, in view of the fact that the processing parameters are commonly used to tailor the initial bitumen composition, the processing and compositional variants are treated here with a microstructural perspective.

The microstructure of bitumen consists of colloidal solid particles of polar aromatics and asphaltenes dispersed in a viscous oil comprised of saturates and naphthene aromatics. This arrangement is the central feature upon which the successes of the many variants rely. Consider a hypothetical bitumen with the composition 5 wt % saturates, 30 wt % naphthene aromatics, 45 wt % polar aromatics, and 20 wt %

¹⁴See Sect. 3.1.3 for descriptions of the atomic, molecular, and microscopic structures of sulfur that make it suitable as a binder.

asphaltenes, which may be taken to represent the compositional ranges cited earlier. Based on mass, this system is 35% liquid and 65% solids. Assuming that the specific volume of each liquid component is conserved when it coexists in the bitumen and invoking the densities given earlier, we find that the average density of the liquid phase is 0.95 g cm^{-3} . Then, based on volume, this system is approximately 44 vol % polar aromatics, 18 vol % asphaltenes, and 38 vol % liquid. The two solids represent 62% of the total volume. This concentration is within the range set by two theoretical particle-packing limits, namely, the concentrations that correspond to the random-loose and the random-dense packings of monosized spheres, which are 59 and 63 vol %, respectively¹⁵ [178]. In view of the fact that the relative total concentration of polar aromatics and asphaltenes is high, these densely crowded dispersed solids can be anticipated to raise the viscosity of the overall bitumen system to a level that greatly exceeds that of the low-viscosity, continuous liquid phase.

This effect of solids concentration on viscosity and the related effects on other rheological properties, such as the shear-dependent and time-dependent flow behaviors, is well known [87,88]. In fact, the yield value of such a system can endow the bitumen with the appearance of a solid, while the dispersion actually contains nearly 40 vol % liquid and the solids are not bonded together. Under the conditions just described, the ability of the bitumen to deform by localized particle rearrangements is greatly restricted. This description is consistent with the fact that bitumen must be heated in order to flow. It also leads directly to an understanding of the fact that bitumen does not possess a melting point but, instead, softens at elevated temperature. This dispersion model also leads to an explanation for the slumping that bitumen exhibits after long age. In other words, the viscoelastic flow of the dispersion underpins the fact that bitumen flows under its own weight, and this phenomenon transforms the solid-like material that is observed in the short term into a fluid or semisolid when the long-term rheological behavior is considered.

¹⁵Although the particle size in bitumen is certainly not monosized, these packing limits may be used as guides in the present example. A denser packing arrangement of particles can persist only if the small particles in the system fit into the voids created by the packing of the larger particles. For the packing of spherical particles in a bimodal mixture, the minimum particle size ratio (i.e., the ratio of the small particle size to the large particle size) that corresponds to the critical, close-packed state is approximately 1:6.5, depending on the assumed packing arrangement [178]. Hence, the diameter of the small particles must be ~15% of the diameter of the larger particles in order for the bimodal system to be close packed. These considerations explain the commonly observed upper limiting range of ~60 to 65 vol % solids for bitumen systems. In other words, bitumen with ~35 to 40 vol % liquid is the norm, and the properties of such a system are governed by the principles of solid-liquid dispersions. The ability to rearrange these concentrated particulates contributes greatly to the behavior of bitumen during processing and storage.

The impact of processing variants on the bitumen and the potential roles of important additives that can be used to tailor the material can be now addressed. As an example of the first case, the temperature at which the volatiles are distilled out of the petroleum crude greatly affects the residual liquid-phase composition [9,10]. With regard to the petroleum crude from a single source (i.e., with an identifiable, fixed composition), a high distillation temperature leads to a more efficient removal of the lower paraffins and naphthene aromatics from the crude than does a low distillation temperature. In turn, the average molecular weight and viscosity of the bitumen are higher for the residue obtained at the higher temperature. Consequently, the bitumen from the high-temperature distillation is more solid-like (e.g., harder, stiffer, and more difficult to soften) than that from the low-temperature distillation [9]. Depending on the applications for which the first type of bitumen is to be used, it may require additives that would induce a lowering of the yield stress and similarly affect other rheological properties, especially those upon which subsequent processing of the bitumen, for example, casting (molding), rely. On the other hand, the properties of the bitumen obtained from the low-temperature distillation may benefit from oxidation procedures, as is the case for air-blown bitumen [9], and the small degree of cross-linking that can then be realized from them. For this material, the procedures that permit cross-linking would lead to a continuous liquid phase that is relatively more viscous. Overall, this bitumen would be stiffer than that obtained from the high-temperature distillation, and, therefore, it would be suited for different applications.

Properties. Bitumen is a complex colloidal system [1,4,9], and its rheological properties reflect a mixture of properties that are attributable to particulate sols and to gels [2]. In particular, micelles appear dispersed in heavy viscous oils (polar aromatic and asphaltene fractions) [1]. The great differences in rheology [2] and relaxation behavior [3] that bitumens can exhibit have been attributed [1,2,9,10] to the different degrees of peptization that exist in these emulsions.

Bitumen is a thermoplastic organic material that is composed of a wide variety of mixtures of high-molecular-weight hydrocarbons that are soluble in carbon disulfide. Based on its temperature-dependent rheology, bitumen may be classified as either a semisolid or a solid [378]. Its overall consistency is sensitive to the proportions of the saturates, naphthene aromatics, polar aromatics, and asphaltenes present [9]. Clearly, the chemical stability of the mixture, the physical arrangement of the different phases, and

the properties that the bitumen exhibits are similarly sensitive to the composition and the mode by which it is processed, including the presence and type of waste species.

Mineral fillers can be added to tailor the flow properties [8,10]. Ground limestone, finely divided silica, and mica are among those used. They help to improve the resistance to flow at elevated temperatures and the impact resistance at service temperatures. The presence of asbestos, which has a fibrous morphology, can help to increase the toughness of the bitumen, in addition to enhancing the other properties just cited.

The thermoplasticity, resistance to water, and adhesion to most substances that bitumen exhibits make it a primary engineering material [9]. Some properties that are critical for its use as a waste-form matrix are its burn point, flash point, homogeneity, ignition point, tendency to separate into component phases, softening point, swelling, thermal conductivity, and viscosity [371,376,377,378].

Cracking and fracture in bitumen are typically caused by a reduced plasticity [10]. This loss generally stems from the composition of the continuous phase in the bitumen microstructure. Specifically, if the concentration of the lower-molecular-weight constituents in the continuous phase, namely, the saturates and naphthene aromatics, is reduced, the plasticity of the overall mixture is correspondingly decreased. The dispersion of high-molecular-weight matter is then less capable of deforming under a load, and cracking or fracture occurs if the effective load exceeds a critical value that is now lower than that for the analogous dispersion with the original composition in the continuous, low-molecular-weight phase. Hence, the bitumen matrix is easier to crack or to fracture.

3.2.5. Thermoplastic Polymers: Vinyl-Based Materials

Raw Materials or Starting Components. Vinyl-based polymers are made using monomers that contain at least one carbon-carbon double bond, C=C, and are generally represented by the formula

where X represents any of a variety of chemical functionalities, of which hydrogen (H-), phenyl (C₆H₅-), halogen (Cl- and Br-), methacrylate [CH₂C(CH₃)C(O)O-], and cyano (N^oC-) groups are among the most common examples. Upon polymerization, the monomers with these X-functionalities lead to polyethylene, polystyrene, poly(vinyl chloride) (when Cl is the halogen), poly(vinyl methacrylate), and polyacrylonitrile, respectively [182,187,188,228,235]. If the X-group is a saturated hydrocarbon moiety, compound (XXI) is termed an α -olefin because the double bond occurs between the terminal carbon. Common examples of the important higher olefins for which X denotes a saturated hydrocarbon unit with the formula C_nH_{2n+1} are 1-butene ($n = 2$), 1-hexene ($n = 4$), and 1-octene ($n = 6$).

Polyethylene is the major member of this family for waste disposal. Ethylene,

when polymerized to yield high-density polyethylene (HDPE), can lead to linear chains that are highly crystalline. The degree of crystallinity exceeds 90%, and less than one side chain is generated per 200 carbon atoms [187]. The nominal density of HDPE is in the range 0.95 to 0.97 g cm⁻³ [187], a value that can vary with the temperature and method of its production, the degree of crystallinity, and the pressure, among other factors [183]. It is a hard and tough material [187].

Ethylene can also be polymerized to yield a product with molecular branching [215]. When the degree of branching is very high, low-density polyethylene (LDPE) is obtained. Typically, a LDPE macromolecule may contain, on a number-average basis, 50 short branches and less than 1 long branch [187]. The degree of crystallinity is greatly reduced in LDPE, as compared with that in HDPE, and is on the order of 50 to 60%. The nominal density of this material is in the range 0.91 to 0.94 g cm⁻³ [187]. Generally, the major differences in the properties of LDPE and HDPE derive from the degrees of branching and crystallinity. For example, each has low permeability to gases, but HDPE is the less permeable of the two grades because the linear material is denser and more crystalline. Polymerization techniques that ensure a predominance of short-chain branches, with virtually no long-chain branches, produce a linear, low-density polyethylene (LLDPE). These techniques focus on the copolymerization

of ethylene and an α -olefin, such as just described [187,215]. LLDPE has unusually good melt-flow and physical properties [187].

Other important vinyl-based polymers are polypropylene, based on propylene,

copolymers of ethylene (XXXI) and propylene (XXXII); polymer blends, which are mixtures of two or more polymers or copolymers; and polymer alloys, which comprise a subset of immiscible polymer blends that are microstructurally heterogeneous [187,213, 220,222,228,243,245].

Many of the homopolymers, copolymers, blends, and alloys consist, at least in part, of vinyl-based polymers for which the X-functionality is not hydrogen. Common ones that have already been cited are poly(vinyl chloride), polystyrene, polymethacrylate, and polyacrylonitrile.

Chemistry and Physics of Process. The fundamental chemistry that underscores the polymerization of vinyl monomers was described earlier in regard to the addition polymerization reaction by which the unsaturated polyesters are cross-linked; see Sect. 3.2.3. This reaction normally involves the generation of the free radical

where the raised dot denotes the free radical and the unpaired electron in this species and the symbol $\sim$ indicates the general nature of the original vinyl site, as described earlier for the species (Sect. 3.2.4). The radical is very reactive and leads to oligomeric and polymeric chains. It combines readily with other free radicals, via routes that permit the unpaired electrons in each to be paired. Then, the addition polymerization of the generic vinyl monomer [i.e., compound (XXI)] produces linear polymers of the type

(XXXIII)

Both homogeneous and heterogeneous processes are used to make vinyl-based thermoplastics [213,235]. These involve four basic techniques: bulk, solution, suspension, and emulsion polymerization [188].

Bulk polymerization may use as few as two components: the monomer and the initiator that generates the free radical species. The polymerization is conducted in stirred reactors or tubular reactors [215,235]. The first type permits discontinuous monomer addition, and the second allows continuous addition of reagents. This approach is limited to low- and medium-molecular-weight regimes because the melt viscosity at the end of the process must be sufficiently low that the product can be removed from the reactor; reactors are typically stirred. Conversion rates for bulk polymerization are generally high.

Solution polymerization is carried out in the presence of a solvent, and, in view of the fact that the solubility of the polymer produced may differ from that of the monomer, the system may become heterogeneous as the polymerization proceeds [188]. The presence of the solvent permits polymers of high molecular weight to be made. For instance, high-molecular-weight poly(vinyl acetate), poly(vinyl alcohol), and copolymers of vinyl acetate and ethylene may be prepared via solution polymerization procedures [235]. As for bulk polymerization, solution polymerization may also be conducted either discontinuously (e.g., in stirred reactors) or continuously (e.g., in tubular reactors).

Suspension polymerization is sometimes used with monomers that are insoluble in water [188]. Here, the monomer (e.g., vinyl acetate) is suspended in an aqueous medium, and drops in the micrometer-to-millimeter size range are generated. Dispersing agents are used to ensure that coalescence does not occur and that the two-phase system remains sufficiently stable during processing [217,235]. An oil-soluble initiator is used. This arrangement permits the monomer drop to behave as a miniature bulk polymerization system [187,188]. This approach produces polymer beads that can be easily separated from the remainder of the mixture [235]. Suspension polymerization combines the advantages of bulk and solution techniques: that is, the removal of the generated heat during the polymerization stages is straightforward, the product can be easily isolated and handled, and the polymerized product is free of solvent. However, the need to wash the polymer free of additives may be considered a disadvantage of

this approach [188]. Important processing parameters, such as the nature of the suspending (dispersing) agent, the reactor design, and the stirrer speed, affect the stability of the heterogeneous, two-phase system and the particle size distribution of the beads [235].

Emulsion polymerization differs from suspension polymerization, although the two techniques have some features in common [187,188,213]. Emulsion polymerization involves the dispersion of oil drops in aqueous media. This dispersion is the emulsion, and water is the continuous phase. Water-insoluble monomer is used, and this aspect is one shared with suspension polymerization. Still, significant differences exist. For emulsion polymerization, a water-soluble initiator is used, the polymerization occurs in particles whose dimensions are in the nanometer size range, the emulsifying agents (viz., soaps and detergents) play key roles in the process, and the kinetics of the process differ considerably from those of suspension polymerization [187,188,214].

Emulsion polymerization is the most important for the production of vinyl ester homopolymers and copolymers, and discontinuous polymerization, carried out in stirred vessels, dominates the industrial use of this approach [235]. The emulsions are typically used in liquid form, but they may be spray dried to yield powders that can be redispersed in aqueous media. The stabilizer or surface-active agent that helps to ensure emulsification is a critical component in the process. This component may be a water-soluble, polymeric protective colloid, an anionic emulsifier that contains hydrophilic and hydrophobic groups, or a nonionic emulsifier with hydrophobic groups and hydrophilic polyether chains [188,235]. Examples of these protective colloids used as such additives are poly(vinyl alcohol), hydroxyethyl cellulose, and starch. Typical anionic emulsifiers include sodium dodecylsulfate, also known as sodium laurylsulfate; dodecylbenzene sulfonate; and dioctyl sulfosuccinate. Lastly, oxyethylation products of nonylphenol, fatty alcohols, and poly(propylene oxide) represent the nonionic emulsifiers.

Particle size of the polymer is affected by the choice of emulsifier [188,235]. For instance, protective colloids yield emulsions with an average particle size of approximately 1 to 10 μm , whereas ionic emulsifiers lead to a particle diameter of 0.1 to 0.3 μm . Sometimes, the emulsifier enters into the polymerization (i.e., in addition to playing a central role in the stabilization of the two-phase emulsion); this trait has been described for poly(vinyl alcohol) in the emulsion polymerization of poly(vinyl acetate) [235].

After the polymer resin is made, further processing includes the shaping and melt stages, among others [187]. Here, we shall focus on the melt and its properties. A critical aspect of the molten state is the form adopted by the polymer. The molten-state density of essentially linear polymers with relatively few carbon atoms per molecule, say 500, is nearly the same as that for much larger ones with 10^5 or more carbon atoms [179]. The molten-state density is, moreover, of the same order as the density of crystalline hydrocarbons [179]. Consequently, the chain segments in the molten state must be very close to one another. Neutron scattering experiments indicate that the molecules in the melt can exist as individual coils, in a fashion related to the conformation adopted in dilute polymer solutions [179]. For example, in dilute solutions, polyethylene that contains 10^5 carbon atoms and a molecular mass of 1.4×10^6 is coiled and occupies 13% of the available volume, and the solvent occupies the remaining 87%. In the molten state, the chain segments of neighboring polymer molecules fill the apparent "empty" space associated with a single coil. Hence, the intermolecular forces between neighboring molecules are very similar to the intramolecular forces that help to stabilize the coiled state.

This state of interpenetrating polymer molecules sets the stage for addressing the flow behavior observed in melt processing. The chains must flow through and around one another and must stretch, deform, and retract in order for flow to occur. Collectively, these movements are the source of the resistance to flow that characterizes polymer melts. Thus, the chemical architecture of the molecules and the molecular arrangements in the polymer melt greatly contribute to the rheology and to other properties of this state.

The ability of the molecules to move, as just described, is sensitive to temperature. At temperatures that greatly exceed the melting point (T_m), the polymer is a viscous liquid under conditions of low shear rate ($\dot{\gamma}$). Molecules form and break entanglements, and the times required to establish these and to dissolve them are short, that is, as compared with the characteristic time associated with the shear (t_e , given by $\dot{\gamma}^{-1}$).

Consider the changes that occur as the temperature is lowered from this set of conditions, while the shear rate is maintained constant. The mutual entanglements among neighboring molecules become more stable because Brownian motion, which depends directly on temperature, is reduced. Then, after sufficient cooling, the lifetime of entanglements exceeds t_e , and the entanglements act as local, physical cross-links between chains [179]. Under these conditions, the melt is a viscoelastic liquid and resembles an

elastomer. However, a significant difference is that these virtual cross-links in the melt are transient, whereas those in an elastomer are permanent.

Upon further cooling, the number of physical cross-links increases. The ability of the polymer molecule to rotate about the C-C bonds is greatly reduced. Then, a great energy barrier exists regarding the relative movement of chain segments, and the elastic modulus of the melt can increase two or three orders of magnitude over the temperature range of a few tens of degrees, as cooling continues. Under these conditions, the melt behaves as a viscoelastic solid [179]. The transition in properties from those of a viscoelastic liquid to those of a viscoelastic solid occurs near T_m .

Lastly, as the cooling continues, the rotation about the C-C bonds becomes essentially impossible. The material is then hard and often brittle. At a critical temperature that depends on many factors, including the chemical composition and the cooling rate, the specific volume of the polymer discontinuously changes, and the polymer is in a glassy state. This phenomenon and the properties of the glass transition regime (T_g) are described more fully in Sect. 3.3. Although the polymer is in the glassy state, it may contain crystalline regions, as described earlier.

For typical amorphous polymers, the effect of temperature at a constant rate of deformation or shear is equivalent to the effect of deformation or shear at constant temperature [179]. Polystyrene typifies these materials. On the other hand, when the polymer is partially crystalline in the glassy state, the transition from the behavior of a viscoelastic liquid to that of a viscoelastic solid occurs over a much smaller range of temperature. Polyethylene exemplifies these thermoplastics.

Common Variants. Many chemical variants are, of course, possible. Most are outside the scope of this report. However, one family is relatively important and is noteworthy. It is the acrylic family, members of which have the general formula

where X normally represents hydroxy (-OH) and amine (-NH₂) groups. The corresponding monomers are acrylic acid and acrylamide, respectively. Homopolymerization of these monomers produces, in turn, poly(acrylic acid) and polyacrylamide.

Other members of the acrylic family include those that have a methyl group on the other vinyl carbon. These monomers have the general formula

where X is, again, the hydroxy (-OH) or amine (-NH₂) group.

Properties. The vinyl-based polymeric matrices are almost always glassy and amorphous [175,176,179,187,188]. However, they may contain crystalline regions if a high degree of stereoregularity exists in the polymer [175,176,179,187,188,232,237,251].

The main processing factors that affect the fabrication of vinyl-based matrices are the flexibility of the chain and the steric aspects of packing. These factors affect the glass transition temperature (T_g), that is, the temperature range that is characterized in the solid state, upon heating, by the onset of viscoelastic properties and is characterized in the liquid state, upon cooling (T_m), by the discontinuous change in the specific volume of the polymer. The flexibility of the chain and the steric aspects of packing also affect the melting point. As a consequence of this correspondence between the intermolecular and intramolecular factors, T_g and T_m are often simply related [187]. For many vinyl-based polymers, T_g is approximately $(0.6-0.8)T_m$, when the temperatures are absolute values and expressed as degrees kelvin [179].

Effects of molecular weight and chemical architecture are closely tied to those of chain flexibility and packing. Symmetry also becomes an important aspect of the chemical structure and the ability of the chains to move, including to rotate, in the molten state [187]. The T_g values of a copolymer often reside in the temperature range established by the T_g values of the individual homopolymers [187].

Similarly, the effects of branching are understood in terms of the free volume, as indirectly stated earlier in this section for the volume occupied by linear polymers in the melt. Increased branching increases the free volume of the polymer molecule and, thereby, lowers T_g ; namely, it is more difficult for the branched-chain segments to establish the virtual cross-links described earlier at temperatures for which the linear analogs mutually interact and restrict their relative movement.

Chemical cross-links would be anticipated to affect T_g similarly [179,187]. Extensive cross-linking changes the matrix to a thermosetting polymer; however, vinyl-based polymers with small degrees of cross-linking would retain many of the thermoplastic properties that underscore melt processing, the development of the solid-state microstructure, and the ultimate properties of the material.

With regard to the solid-state microstructure, the principal features relate, at least partially, to the degree of crystallinity. Amorphous polymers have a microstructure that closely resembles that of the liquid state in the melt. This resemblance includes the overall conformation and the specific configurational aspects of tangles and intermingled chains. The amorphous microstructure is that obtained upon supercooling and freezing the liquid state. The structure in the bulk of amorphous polymers resembles a long-range agglomeration of closely packed, randomly coiled spaghetti [179]. This microstructure leads, for instance, to elastic properties that reflect the short-range rotation of the C-C bonds. Young's modulus, for instance, is relatively low, being in the range of 2 to 4 GN m⁻² at 300 K (i.e., 27°C).

Linear polymers, such as polyethylene, form crystals with a folded-chain structure that resembles, in many features, macroscopic corrugation. The dimensions of the lamellae are on the order of 10 to 20 nm, requiring that the chain be folded many times along its length, which may exceed 1000 nm [179]. This microstructure often leads, in turn, to properties that reflect the ordered state. Compared to the amorphous analogs, these polymer matrices exhibit high values of Young's modulus. Highly oriented polyethylene has a modulus on the order of 100 to 200 GN m⁻² at 300 K. It is noteworthy that the degree of crystallinity is generally inversely related to the cooling rate and that this relationship has also been observed for reinforced thermoplastics [241].

The properties of semicrystalline polymers derive features from both types of regions. In the case of elastic modulus, it is dominated by the elastically weaker amorphous regions. Hence, highly crystalline polyethylene typically possesses a Young's modulus less than 5 GN m^{-2} at 300 K.

These microstructurally derived considerations directly affect the fracture behavior of these materials. For instance, consider polyethylene, which has a T_g value of 188 K (i.e., -85°C), and polypropylene, which has a T_g value of 278 K (i.e., 5°C), when each is subjected to an impact at large load but over very short duration and under subzero temperature conditions, say -20°C [179]. Being above its transition temperature, the microstructure of polyethylene is capable of chain movement that can keep pace with the transmission of the shock. The polymer remains ductile. Contrasting this situation, the microstructure of polypropylene is below its transition temperature, and relative chain movement is severely restricted. The microstructure of this material cannot keep pace with the transmission of the shock. Cracks develop rapidly, and this polymer readily fractures; that is, it is characterized as brittle. As a result of these phenomena, polyethylene is used in underground piping for gas and water [179].¹⁶ Furthermore, owing to its properties at this and similarly low temperatures, polyethylene can be welded [227].

Summarily, the concepts developed in this section reveal that the microstructure of the melt establishes the microstructure of the solid for a constant set of processing conditions. Amorphous, crystalline, or semicrystalline polymers may result upon melt processing. The precise phase composition depends on the chemical aspects of the polymers—such as molecular weight, branching, steric hindrance of chains upon their mutual close approach, and their contributions to the glass transition regime—and the processing variables, such as the cooling rate (described more fully in Sect. 3.3). In the case of polymer blends, the degree of miscibility can rule [252], governing the types of phases present in the final solid polymer. The properties of the solid matrix are intimately linked to such factors and to changes in the microstructure as the external conditions change. This relationship also holds for toughened thermoplastics, such as phenolic resins [238,239].

¹⁶Alternatively, reinforced thermosetting polymers, which are not ductile, can be used [91].

3.3. Vittrified Matrices

The principal vitrified matrices listed in Table VII that have been used or proposed to be used as final waste forms are inorganic glasses that are primarily based on silica (SiO_2) or phosphorus pentoxide (P_2O_5) [443,452,454]. The glasses based on silica can be categorized according to the type of anion present [118,124]. Chalcogenide glasses are those that contain anions of Group 16 (VI A) elements of the periodic table. These elements are oxygen, sulfur, selenium, and tellurium. Halide glasses contain anions from Group 17 (VII A) elements: fluorine, chlorine, bromine, and iodine. Oxide glasses are a subset of the first category, the chalcogenide glasses. But, owing to the large size of this family, oxide glasses, such as those of SiO_2 and P_2O_5 , are often considered separately from the other chalcogenide glasses. These oxides form glasses without the addition of other chemical agents, and, hence, they are known as primary glass-forming oxides [111,124]. Still, the glasses based on these two oxides may contain species derived from other oxides. If these additional oxides are capable of contributing over 50 atom % of the cations in a glass, they are classified as conditional glass formers. Common examples of these compounds are oxides of iron, aluminum, gallium, bismuth, beryllium, and lead, among others [111,124]. They may be used to prepare specific silica-based and phosphate-based glasses. Fluoride glasses are the most important halide glasses. Beryllium fluoride is the principal glass former for these materials [107], whereas the fluorides of many metals that often reside in hazardous and mixed wastes (e.g., zirconium, thorium, uranium, scandium, yttrium, chromium, aluminum, gallium, indium, zinc, cadmium, and lead [124]) are conditional glass formers.

Other types of glasses include oxyhalide, oxynitride, and oxycarbide glasses and are discussed later. However, a few of their salient features are noteworthy here. The presence of halides, nitrides, and carbides significantly alters the processing properties of the corresponding additive-free glasses and, more importantly, affects the properties of the final glasses produced. Other additives, such as carbonate, nitrate, sulfate, dichromate, and selenate anions are microstructurally characterized as having inefficient packing of the anionic species in the glass. This property relates to the unbalanced force fields surrounding the cations in the glass. Such systems may possess very low T_g values, sometimes near or below 0°C [124]. Moreover, these glasses typically exhibit a low resistance toward attack by water. Thus, the presence of these additives may increase the water solubility of the glass.

Clearly, the range of pertinent topics that can be discussed in terms of the use of vitrified matrices based on silica and phosphorous pentoxide is broad. As a consequence, the following discussion emphasizes the salient features of these matrices and their fabrication. The principal concepts that are described in this section for vitrified matrices are summarized in Table XI. Organic polymer glasses [186,187,188,213,220,222] and metallic glasses [127,128,175,176] are not addressed, per se. The factors that affect the viability of these glasses as waste-form matrices are addressed in other sections; see Sects. 3.2.5 and 3.6.

Raw Materials or Starting Components. Glasses are usually formed by solidification from a melt that is derived from silica and various additives [54,73,119,120,124]. For the principal glasses that have been examined as waste forms, the added reagents are typically oxides of alkali and alkaline earth metals, of boron (B_2O_3), and of aluminum (Al_2O_3) [118,443]. The relative concentration of SiO_2 is on the order of 50 wt %. Similarly, for glasses based on phosphorus pentoxide that have been examined as candidate waste forms, the P_2O_5 concentration is also approximately 50 wt % [443].

Chemistry and Physics of Process. Both the molten glass and the solidified glass do not exhibit long-range order on the scale of atomic structure. The short-range order, on the order of a few tens of nanometers, is frequently represented in terms of radial distribution functions [54,108]. Although some glasses may exhibit x-ray diffraction patterns, these patterns typically suffer from broad peaks that are not easily characterized. Glasses are often viewed as three-dimensional networks that lack symmetry and periodicity: that is, they lack a unit of the structure which is repeated at regular intervals.

The melting process converts granular or powdered raw materials into a homogeneous liquid [119,124], which is free from visible defects and can be manipulated in a variety of ways in order to prepare it for forming operations [120]. The overall melting operation consists of three fundamental steps: batch melting, fining, and homogenizing [119]. These three steps occur simultaneously in a continuous glass melter, but distinct stages may characterize periodic processes, such as those used with pot tanks.

Batch melting is the process by which the granular raw materials are converted to a liquid that is essentially free of undissolved crystalline inclusions [119]. Normally, the raw materials are dried and dehydrated. Desired salts are melted, along with low-melting ingredients (i.e., fluxes) that melt in the

range 400 to 800°C. These fluxes can decompose to yield, in part, gaseous products. Then, the dried silica and other refractory materials are dissolved in the molten fluxes.

The viscosity of the molten salts, prior to addition of silica and other refractory components, is very low; values on the order of 1 to 4 mPa·s are typical. Upon dissolution of the refractory components and the accompanying increase in the concentrations of silica and alumina, anions begin to decompose. This process can be accompanied by the generation of large volumes of gaseous products (e.g., CO₂, H₂O, N₂, O₂, and SO₂), whose volume may be much greater (e.g., two orders of magnitude greater) than that of the melted batch [119]. The release of these gases agitates the melt, thus increasing the dissolution rate of the remaining refractory components. Dissolved silica raises the viscosity of the melt by approximately four orders of magnitude, and values of viscosity in the range of 10 to 40 Pa·s are common.

The fining process is one in which the bubbles are removed. Additives that contain sulfate species can facilitate the removal of bubbles via the generation of SO₂ at elevated temperatures [119]. The coalescence and growth of bubbles are key aspects of their removal.

The homogenizing step consists of the elimination of chemical and thermal variations in the molten glass [119]. Compositional variations produce defects in the final product, and temperature variations lead to less-than-optimal processing and losses during the forming stages. Of these two problems, the compositional variations are the more difficult to eliminate or to minimize [119]. Chemical inhomogeneities result from segregation of components during the melting process, loss of volatile intermediates near the surface of the melt, and reaction between the melt and the refractory materials added.

The molten liquid is poured into a mold and subsequently cooled [120,124]. The structure of the molten glass changes as the cooling proceeds. The composition, the relative amount of various chemical phases, and the degree to which a network permeates the melt depend on the temperature, among other factors, and they generally change during the cooling process [113,114]. As the temperature decreases, the liquid densifies, and atomic movements are more difficult. The increased atomic packing means, in turn, that the movement of one atom requires the cooperative movement of neighboring atoms. As the cooling proceeds, the ability of the structure to rearrange is hindered by the molecular arrangement within the

molten glass. Clearly, the structure of the liquid phase is distinguished from that of the solidified glass by the degrees of atomic and molecular mobility, with these being greater in the liquid phase. The relaxation of the molten glass structure occurs at the rate of cooling, q ($\equiv dT/dt$, where T and t denote the temperature and time, respectively). This relationship means that the time required for a structural rearrangement, t , in response to the temperature change, ΔT , is much shorter than the time the molten glass spends between temperature T and $T+\Delta T$ during cooling. Then, $t \ll \Delta t$, where Δt is given by $\Delta T/q$, and equilibrium prevails, relieving local mechanical stresses and eliminating chemical gradients in the glass specimen [114]. On the other hand, if $t \gg \Delta t$, mechanical stresses that can lead to fracture of the glass remain, and chemical gradients can survive the cooling process and lead to subsequent chemical transformations, including devitrification.

Upon cooling, crystallization may or may not occur [54,109]. If it does, a discontinuous change in the volume occurs at the crystallization temperature, which is commonly equated to the melting point, T_m ¹⁷ [109]. Then, the coefficient of expansion, α_v , namely, the differential change in volume, V , with a change in temperature, T (i.e., dV/dT), abruptly changes discontinuously from the value for the liquid, $\alpha_{Vliquid}$, to that of the crystalline material. However, if crystallization does not occur, the volume of the liquid decreases at approximately the same rate as it does above the melting point (viz., $\alpha_{Vliquid}$). This process proceeds until there is a continuous decrease in the expansion coefficient over a temperature range, known as the glass transformation range. In this range, $t \approx \Delta t$, indicating that relaxation processes may or may not occur in step with the cooling rate, q . This relationship between the structural rearrangement and the temperature underpins the kinetic aspect of the glass transformation range. Using the coefficient of expansion as the central property under consideration, the glass transition temperature, T_g , is taken as the temperature below T_m at which the coefficient of expansion for the solid-like glass, α_{Vglass} , deviates from $\alpha_{Vliquid}$. Equivalently, it is the temperature at which the volume-temperature profile for the glass intersects that for the supercooled molten glass liquid.

The value of T_g is sensitive to the cooling rate, q , in addition to the chemical properties of the system. For instance, this transformation range is $\sim 120^\circ\text{C}$ for a soda lime-silicate glass when the q is 1°C s^{-1} , and it

¹⁷The description provided here is based on volumetric changes with cooling. Other physical properties, such as specific heat, refractive index, and electrical resistance, can also be used as the central feature of the discussion [112]. See Ref. [112] for a description of the effects of cooling rate on glass properties, as well as its influence on annealing behavior.

is $\sim 220^\circ\text{C}$ when q is $10^4^\circ\text{C s}^{-1}$ [114]. Likewise, the more rapid cooling rate yields a higher T_g value [54,112]. As a rule, the reduced glass transition temperature, T_{rg} ($\equiv T_g/T_m$, where the T values are expressed as absolute temperatures), is approximately 2/3 for simple molecular substances that easily form glasses in bulk, and it is less than 2/3 for those substances that do not readily form glasses [109]. Lastly, the glass structure does not relax at the rate of cooling for temperatures below the transformation range, reflecting the fact that $t \gg \Delta t$. Then, atomic and molecular rearrangement is not possible because the liquid has become a glass [54,113,114].

The forming process can be either straightforward or complicated [73,120]. The glass transition temperature and the temperature-dependent viscosity are central to forming processes [73,113,114]. Melt processing offers the options for shaping, with little porosity remaining in the final product. Casting, drawing, blowing, and spraying techniques exist [73]. The details of these processes are beyond the scope of the present report. However, the central role of viscosity and its reliance on atomic structure demand that the structural aspects of glasses be examined here. Alternative methods by which glasses can be made involve condensation from gaseous, liquid, or solid solutions [109]. The condensation is induced on surfaces held well below the T_g temperature of the condensing material, and the deposition rate must be sufficiently low that the heat of condensation does not heat the condensate above T_g [109].

As stated earlier in this section, both the molten glass and the solidified glass do not exhibit long-range order on the scale of atomic structure, but they may possess short-range order, on the order of a few tens of nanometers. In view of the fact that they lack a unit of the structure that is spatially repeated at regular intervals, as would be the case for crystalline materials, the three-dimensional molecular networks comprise the chemical structural units of interest here. In oxide glasses, oxygen polyhedra establish these networks [54]. Three general rules apply to many oxide glasses [54,103,107,112,124]: (1) each oxygen ion should be linked to not more than two cations; (2) the coordination number of oxygen ions about the central cation must be small (e.g., 4 or less); and (3) oxygen polyhedra share corners, not edges or faces, and at least three corners of each polyhedron should be shared. In practice, the glass-forming oxygen polyhedra are triangles and tetrahedra, and the cations that form such coordinated polyhedra are network formers [54]. Vitreous SiO_2 and B_2O_3 satisfy these rules [107,112,124], and the cations in these systems are Si and B, respectively. Alkali silicates form glasses easily, and the silicon atoms are the network-forming cations. The alkali ions have the principal function of providing additional oxygen ions

that modify the network structure; thus, the alkali ions are considered network modifiers [54,107,112]. Cations that have higher valence and lower coordination number than the alkali and alkaline earth cations (e.g., Ti, Zn, Pb, Zr, and Cd, [54,112]) may also contribute to the network structure; these species are referred to as intermediates. Generally, the role of the cations depends on their valence and their coordination number.

Although these principles described here may be considered as guidelines, the formation of glasses and the similarity of the structure of glassy oxides and their crystalline counterparts derive from kinetic factors: that is, the kinetic factors related to the ability or inability of the glass structure to rearrange during processing seem to play more important roles than do the chemical rules just identified [54]. Still, the latter constitute useful guidelines for similarly processed glasses [124].

With this relationship in mind, we turn to the three major categories of glasses that pertain to waste disposal: silica-based glasses, borate glasses, and phosphate glasses.

Silica glass is composed of a random network of SiO_4 tetrahedra, and there is significant variability in the Si-O-Si bond angles [54,107,112]. This network is not necessarily uniform, and local variations of the density and structure are anticipated. Addition of alkali or alkaline earth oxides to SiO_2 increases the ratio of oxygen (anion) to silicon (cation), producing a value greater than 2. This alteration breaks the three-dimensional network, producing singly bonded oxygen atoms that do not contribute to the network [54,107]; concomitantly, the added cations occupy "holes" in the structure where the network is broken [124]. Instead, the oxygen helps to neutralize the ionic charge of the additional cations. This altered structure is referred to as a silicate glass. Using the crystalline analogs to the glasses with ratios higher than 2, the structural units in various silica-based glasses can be surmised [54]. With an O-to-Si ratio of 2, SiO_2 may be considered the reference system. It has a three-dimensional network, as already explained. The crystalline counterpart of this glass is quartz. A ratio of 2.5 (viz., Si_4O_{10}) leads to sheets as the structural units, such as those found in talc. A ratio near 3 (e.g., Si_4O_{11} and SiO_3) leads to chain-like structural units—resembling those found in amphiboles (which have double anionic chains of Si_4O_{11} units) and pyroxenes (which have single anionic chains of SiO_3 units)—and ring units, such as in beryl [54]. As the ratio exceeds 3, tetrahedra that share one oxygen ion (e.g., Si_2O_7) and isolated orthosilicate tetrahedra (SiO_4) are favored as the structural units.

Vitreous B_2O_3 is composed of BO_3 triangles that are linked in a boroxyl configuration [54,107]. Addition of alkali or alkaline earth oxides to B_2O_3 results in the formation of BO_4 tetrahedra. Up to approximately 30 mol %, nearly all of the modifier oxides effectively convert the BO_3 triangles to BO_4 tetrahedra. At concentration levels beyond this value, singly bonded oxygens are present throughout the borate glass.

Phosphate glasses resemble silicate glasses in that they are also composed of oxygen tetrahedra [54]. However, unlike the structural units of silicate glasses, those of phosphate glasses contain a PO_4 tetrahedron that can bond, at most, to three other similar tetrahedra. This limitation, derived from bonding requirements, means that phosphate glasses are primarily composed of rings or chains of PO_4 tetrahedra. Addition of alumina can lead to properties in phosphate-based glasses that simulate those in network-based silicate glasses [54].

Common Variants. Of course, combinations of the components implied by the examples already discussed can be usefully processed to yield glasses of various properties. For instance, borosilicate glasses can be made by incorporating B_2O_3 into a SiO_2 -based melt. Proportions for $B_2O_3:SiO_2$ of 1:3 and 1:4 typify the glass compositions that have been studied as waste forms for radioactive waste [443].

Other types of glasses include oxyhalide, oxynitride, and oxycarbide glasses [124], as Table XI indicates. The oxyhalide glasses contain both oxide and halide anions. The presence of halides in these glasses typically has the effect of reducing the glass transition temperature, T_g , and increasing the coefficient of thermal expansion, that is, compared with the values for the halide-free compositions. Oxynitride glasses can be prepared by adding small concentrations of nitride ions to an oxide melt (e.g., as Si_3N_4 or AlN). These additions often increase the viscosity of the melt; the refractive index, T_g ; and the hardness of the glass. Oxycarbide glasses are prepared by adding SiC to the melt. The values of T_g and hardness are increased beyond those found for comparable nitride additions [124]. The carbide anion results in a greater degree of cross-linking in the glass. Consequently, the density, elastic modulus, and fracture toughness increase with increasing carbon content.

Properties. The microstructural features of glasses are intimately linked to their chemical composition. However, the processing of the melt is critical in determining the glass transition regime. The cooling rate

is especially important. This parameter controls much of the macromolecular arrangement and the relative ability of the various species to migrate throughout the system.

Many of the properties of glasses derive from the same principles described earlier for vinyl-based polymers (Sect. 3.2.5). For example, the relative difficulty of movement of molecules in the melt greatly contributes to the establishment of the glass transition regime. The glasses discussed in the present section are also extensively cross-linked, a feature that endows them with some of the solid-state properties described earlier for the thermosets; see Sects. 3.2.1, 3.2.2, and 3.2.3. The major one for the present purposes is that mobility of the chain is restricted to short ranges. Consequently, the microstructures of the cross-linked polymers described earlier and that of the glasses described in the present section permit little deformation. Hence, these matrices are brittle [181]. Moreover, they can be anticipated to encapsulate wastes with which they cannot chemically bond on an extensive scale.

The rheology of glasses reflects the fact that they are supercooled liquids, rather than amorphous solids. The glass melt typically exhibits high values of viscosity, exceeding 10^{14} Pa·s [112,113,114,179]. Such viscosity levels reduce the mobility of species and, thereby, their ability to nucleate crystalline phases. Additionally, the thermodynamically stable crystalline phases are often very complex. Hence, nucleation of new phases in an inorganic glass is normally difficult and is associated with a large activation barrier.

Nonetheless, an important property of glasses is that they can exhibit the ability to devitrify. In these cases, polycrystalline microstructures result. Sometimes, devitrification spontaneously occurs upon cooling [73]. The compositions for which this is a likely process contain high concentrations of alkali or alkaline earth oxides that act as modifiers within the larger silicate network [54,176]. These species break the network locally, as described earlier. Then crystallization can occur in the melt as it cools. The alkali and alkaline earth cations occupy the interstices in the network and provide local electrical neutrality. The consequences of this microstructure are an increased tendency toward crystallization and devitrification, a lower softening temperature, and a decreased melt viscosity [54,176].

Some additives, such as alumina (Al_2O_3) and lead oxide (PbO), can act as either network formers or modifiers. They usually decrease the tendency toward devitrification [176]. These systems can be formulated to provide high degrees of chemical resistance [180].

Inorganic oxide glasses can also be prepared using sol-gel technology [65,79,115,116, 122,125]. This approach generally begins with organometallic compounds [177], which are discussed in Sect. 3.4. Siliceous gels contain an extensive siloxane (i.e., $-\text{Si}-\text{O}-\text{Si}-$) network, and this network has an abundance of silanol groups (i.e., $-\text{SiOH}$) [65,122].

A critical step in the production of glasses using sol-gel technology is the drying stage. Extensive shrinkage occurs with siliceous gels during this stage [65,79,122]. The highly branched gels are quite flexible, but they become more rigid as the network dries. Supercritical drying techniques can be applied successfully in order to produce large aerogel structures [122].

3.4. Devitrified Matrices

Glass-ceramics are the devitrified matrices emphasized in Table VII. They are produced by the controlled crystallization of glasses with appropriate compositions [54,74,104,137,138,140]. Ordinarily, glass-ceramics consist of very small (i.e., less than $1\ \mu\text{m}$) crystals that are separated by residual glassy phases, and they are free of pores. The relative concentration of crystals is greater than 50 vol %. The degree of crystallinity, based on mass, is greater than 90% and can be as high as 98 vol %. Forming is conducted via conventional glass-fabrication techniques [73,119,120,124]; see Sect. 3.3.

First, a glass is made [140]. This glass is then heat treated to induce the nucleation of usually amorphous phases and their subsequent conversion to the desired crystalline phases: that is, the glass is devitrified. Unlike the devitrification processes that can accompany the fabrication of glasses, which initiate at external surfaces [54,73] and start with a few critical nuclei [134], the devitrification processes used in order to make glass-ceramics are conducted under well-controlled conditions that permit a large and uniform density of nuclei to be generated. This density is on the order of 10^{12} to 10^{15} nuclei per cm^3 . In order to produce such a plentiful nucleation, nucleating agents are used, and the heat treatment is adjusted to nucleate new phases simultaneously throughout the glass [140].

The three central variables in the design of glass-ceramics are the selection of the glass composition, the generation of the glass-ceramic assemblage, and the tailoring of the crystalline microstructure [137,138,140]. The glass composition governs, to a great degree, the workability of the materials

produced. In turn, the workability is largely determined by the glass viscosity, the ease of nucleation, and the rate of crystallization. The phase assemblage, namely, the types of crystals and the relative proportions of crystals to glass, determines many of the physical and chemical properties of the final product. The nature of the crystalline microstructure, that is, the crystal size distribution and the crystal morphology, is central to the mechanical properties of the final glass-ceramic [140]. Similarly, the composition of the crystalline phase, as well as the composition, amount, and morphology of the glassy phase, affects the degree of chemical stability and the durability of glass-ceramics [137]. These steps and the more important concepts of the fabrication of glass-ceramics that appear relevant to waste disposal technology and the issues considered herein are summarized in Table XII.

Raw Materials or Starting Components. Common glass-ceramics are based on mixtures of alumina (Al_2O_3); silica (SiO_2); and alkaline oxides, such as lithia (Li_2O); or alkaline earth oxides, such as magnesia (MgO). In some instances, MgO and zinc oxide (ZnO) are partially substituted for Li_2O , in order to improve the workability characteristics of the glass.

Nucleating agents are typically oxides, such as titania (TiO_2), zirconia (ZrO_2), stannic oxide (SnO_2), chromium(III) oxide (Cr_2O_3), and ferric oxide (Fe_2O_3). These are especially useful when the crystallization of β -quartz is desired [140]. However, metal colloids can aid nucleation [106,137], and they are used, for example, to prepare colored glass-ceramics for decorative applications and colored glasses for light filters [140].

Chemistry and Physics of Process. Glass-ceramics can be made using either bulk or powder processing. The bulk processing of glass-ceramics involves the melting of starting materials, as described earlier in Sect. 3.3. Most of the forming methods cited in that section can be used to make glass-ceramics. These include casting, among others [180].

Following the forming process, the material is heat treated to induce and to control nucleation and crystallization processes. Both the nucleation and the crystallization steps are well controlled. Note that they occur under different thermal conditions and at different ages. Sometimes, the thermal cycle is designed so that both stages occur while the temperature is increased [140].

Conventional powder processing techniques [48,55,64,73] can be used to make glass-ceramics from powdered glass. Examples include extrusion, spraying, and casting procedures. Here, the nucleation and crystallization processes initiate at the surfaces of the glass grains, and the glass sinters via viscous mechanisms [49,50,51,54] just prior to the completion of the crystallization stages. The final product is essentially the same as that made via bulk processing [140].

The glass-ceramics can be further processed using various techniques, in order to strengthen the material [180]. The tailored strength of such materials derives from the inherently greater resistance to crack propagation that is imparted to the material by the polycrystallinity and the microstructure.

These features suggest that the mechanical and other physical properties can be regulated by controlling the microstructure, especially during the thermal treatment stage. Unlike conventional ceramics, glass-ceramics possess essentially zero porosity. Also, their uniform microstructure ensures that the physical properties of the final component are highly reproducible [140]. They can also be tailored to provide a wide range of thermal expansion requirements, excellent thermal shock properties, dielectric properties, and chemical durability, in addition to the mechanical properties of high strength and hardness.

The key to the manufacture of glass-ceramics is composition [54,140]. It must be one that can form glasses and from which crystallization can be controlled. Whether or not this restriction limits their uses as final waste forms depends on both the properties of the matrix phases and the waste to be treated for disposal. Together, these two sets of properties establish the composition ranges for useful glass-ceramic matrices.

Aluminosilicate glass-ceramics are based on a network of aluminosilicate tetrahedra. The members of the lithia- and magnesia-based glass-ceramic families cited earlier have such a chemical microstructure. The lithia-based aluminosilicate materials contain either β -quartz or β -spodumene (β -LiAlSi₂O₆, which can be thought of as Li₂O·Al₂O₃·4SiO₂) as the ceramic phases. An important subset of the magnesia-based materials is β -cordierite (2MgO·2Al₂O₃·5SiO₂) glass-ceramics. Aluminosilicate glass-ceramics that are made with both lithia and magnesia have thermal expansion coefficients that can be tailored and, in some cases, be made negative. These materials can be chemically strengthened. The important crystalline phases are modified β -quartz solid solutions [54]. Clearly, an essential feature of these and other

glass-ceramic families is that desired properties and combinations of properties may be obtained by a systematic variation of the chemistry and the processing of the glass-ceramic compositions, including the variables that have greatest impact on the development of microstructure. This concept applies to both the crystalline phases and the final glassy phases.

The absence of porosity in glass-ceramics derives from the relatively small volume changes that occur upon crystallization, coupled with the fact that volumetric changes can be accommodated by flow of the glassy phases [54]. Moreover, the generation of crystalline phases may occur by spinodal decomposition [54,58,137], rather than by the nucleation and growth mechanisms that underpin most of the preceding discussion. Here, infinitesimal fluctuations in the composition may make a system unstable within the spinodal region. Then the melt separates into two immiscible liquids that are interconnected. Under such circumstances, the generation of interconnected ceramic and glassy phases may result as the mixture is cooled [137]. Such behavior has been reported for borosilicate glasses containing 67.4 wt % SiO_2 , 25.7 wt % B_2O_3 , and 6.9 wt % Na_2O [54] and those prepared commercially via the Vycor process with the approximate composition 75 wt % SiO_2 , 20 wt % B_2O_3 , and 5 wt % Na_2O [54,58].

Common Variants. In addition to the chemical variants within the families represented by the examples provided earlier in the present section and in Sect. 3.3, variants based on the morphology of the ceramic phase are possible. The variant morphologies considered here are sheet-like and chain-like silicate based.

Silicate glass-ceramics that contain crystalline phases with a sheet-like chemical microstructure belong to the mica family [140]. Common commercial glass-ceramics with sheet-like ceramic phases contain fluorophlogopite ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$) or tetrasilicic fluoromica ($\text{KMg}_{2.5}\text{AlSi}_4\text{O}_{10}\text{F}_2$). These materials exhibit unique mechanical properties that derive from the interlocking of plate-like mica grains [137].

Silicate glass-ceramics with ceramic phases of chain amphibole crystals have a microstructure that consists of randomly oriented acicular or fibrous crystals. Amphiboles are metasilicates whose crystals contain anionic double-chain arrangements of $(\text{Si}_4\text{O}_{11})_n^{6n-}$; in turn, these chains comprise silica tetrahedra [54]. The amphibole grains in the glass-ceramics are, of course, separated by glassy phases. Blast-furnace slags, with the addition of sand and clay, can be used to make inexpensive nonalkaline glass-ceramics, called slagsital [140]. The primary ceramic phases are wollastonite (CaSiO_3) and diopside ($\text{CaMgSi}_2\text{O}_6$),

which reside in the aluminosilicate glass matrix. Interestingly, metal sulfide particles serve as the nucleating agents for these materials.

Other groups of glass-ceramics that are related to slagsital (i.e., the ceramic phase has a chain-like microstructure) are the family based on the amphibole potassium fluororichterite ($\text{KNaCaMg}_5\text{Si}_8\text{O}_{22}\text{F}_2$) and the one based on fluorocanasite ($\text{K}_{2-3}\text{Na}_{4-3}\text{Ca}_5\text{Si}_{12}\text{O}_{30}\text{F}_4$) [140]. The microstructure of the first one consists of interlocked fine-grained rod-like amphibole crystals in a matrix of cristobalite (i.e., high-temperature stable crystalline polymorph), mica, and the residual glass. The first of these has good chemical durability, and the second has potential architectural applications [137,140].

One variant processing technique that contrasts the homogeneous and heterogeneous nucleation routes already mentioned, including spinodal decomposition, is photonucleation [105,106,137]. The initial steps in this approach are designed to fabricate a photosensitive glass that contains dispersed metal ions, such as those of gold, silver, or copper, along with sensitizing ions such as Ce^{3+} , Sn^{4+} , or gold and copper salts. The glass is then irradiated with light of specific wavelength, typically in the range 300 to 350 nm. Upon subsequent thermal treatment, this procedure leads to the separation of metal particles that are distributed throughout the bulk of the glass. These particles serve as seeds for the heterogeneous nucleation of the primary crystalline phases that exist in the final glass-ceramic. This general approach has been used, for instance, in order to obtain glass-ceramics based on lithia and silica [137].

Another processing variant is to prepare glass-ceramics using sol-gel methods [65,137]. Here, two schemes have been developed to prepare the initial glass. In the first one, the destabilization of an aqueous colloidal solution (e.g., silica sol) that is either pure or whose solution phase contains desired metal ions is carried out and leads to a particulate gel. In the second scheme, the hydrolysis involves organometallic compounds, such as those with the general chemical formula

where M represents the metal atom, R is a hydrocarbon moiety, and n denotes the number of $-\text{OR}$ functionalities covalently bonded to the metal. Compounds represented by (XXXVI) are not polymeric,

but the hydrolysis of these compounds and the subsequent condensation polymerization yield an inorganic polymeric gel. Suitably designed mixtures of organometallic compounds that contain the desired metals in their appropriate relative concentrations lead to gels with well-controlled stoichiometry. The gels produced from either method can be converted into xerogels (aerogels) by careful drying. These are then converted to a glass-ceramics upon thermal treatment tailored to each system. Sol-gel methods have been used to make glass-ceramic based on silica, titania, alumina, and boria, among others [59,65,137]. Sol-gel methods based on organosols have also been developed [137].

Lastly, glass-ceramic materials can be sintered to full density [453]. This step provides thermal stability that permits, for example, glass-ceramic seals to be reheated to their soldering temperature without inducing deformation [140]. In these specimens, the degree of crystallinity may be as low as 40%.

Properties. Glass-ceramic materials are polycrystalline solids that contain residual glassy phases. They are made by melting glass and forming it into specimens that are subjected to controlled crystallization. The broad variety of microstructures are achieved via thermally driven devitrification. This effort relies on the regulation of a sufficiently large and uniform number density of crystal nuclei throughout the bulk of the glass. The fine-grained microstructure is tailored by controlling the annealing process.

The properties of a glass-ceramic derive primarily from the physicochemical properties of the major crystalline phases [137]. Based on volume, these grains occupy most of the system. Nonetheless, the glassy phases influence the properties of the glass-ceramic materials. The relative contribution depends on the amount of glass phase present and its morphology. Hence, the microstructural features are critical in establishing the properties that glass-ceramic materials exhibit.

Certainly, the physicochemical properties of the glassy phase depend, in turn, on its composition. This dependence was discussed in Sect. 3.3. Moreover, the nature of the interface between the crystalline grains and the glassy phase contributes significantly to the overall properties. A simple example highlights the reason for this effect. Consider the thermal expansions for the crystalline and the glassy phases. The linear expansion of alumina (Al_2O_3) is on the order of 0.9% when this material is heated from 0°C to 1000°C [73]. The analogous expansion for soda lime-silica glass is approximately the same [54], although it is very sensitive to the processing thermal history established during processing [73]. As a

consequence, if the ceramic phase in a glass-ceramic is essentially Al_2O_3 while the glassy phase has the composition of soda lime-silica glass and if the characteristic processing time during which the temperature changes is long compared with the relaxation time for each of these materials, the two constituents respond to changes in temperature in much the same fashion. However, if the ceramic phase is mullite, whose linear expansion is on the order of 0.5% [54], the two phases that now compose the glass-ceramic (viz., mullite and soda lime-silica glass) respond differently to temperature changes. In this second case, the interfacial bond strength would play a major role in determining whether or not the two phases separate with the formation of cracks. Consequently, the interfacial bond strength would have to be sufficiently high in order for the glass-ceramic system to withstand the concentrated interfacial stresses generated by the mismatch of thermal properties.

The microstructure of glass-ceramic materials is complicated. Still, as these examples suggest, the recognition of the various effects that the chemistry and the processing have on the development of the microstructure can greatly facilitate the design and development of suitable materials. The successful incorporation of waste species into a glass-ceramic matrix similarly depends on the interrelationships among the chemistry, the processing scheme, and the development of the microstructure.

3.5. Ceramic Matrices

The principal ceramic matrices listed in Table VII that have been used or proposed to be used as final waste forms, most often for high-level radioactive waste, are simple oxides, ternary titanates, zirconates, silicates, and phosphates, to name but a few [407,408,412,414,415]. The approach of incorporating radioactive species into these matrices is based on two concepts: that the assemblages of crystalline phases in a ceramic waste form are either thermodynamically stable or metastable and that the constituent species are expected to be immobile for geologic duration under ambient conditions of temperature and pressure [271,412,414]. These circumstances help to ensure that high concentrations of waste could be incorporated into ceramic matrices either in solid solution or as separate grains, while maintaining low aqueous solubility and chemical durability when exposed to corrosive environments.

The general approach adopted here is to restrict the candidate ceramic matrices to those that are essentially oxides and oxygen-based systems. The principal ceramic phase may be a single metal oxide or a multicomponent material. Examples of the first group include alumina (Al_2O_3), rutile ($t\text{-TiO}_2$), zirconia (ZrO_2), and hematite (Fe_2O_3). Members of the second group include mullite, which is an orthorhombic, crystalline aluminum silicate with the formula $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, and members of the spinel family (that is, the class of crystalline refractory oxides with the general formula AB_2O_4 , in which A is a divalent metal or mixture of divalent metals and B is a trivalent metal) [54,60]. Typical compositions within this family are represented by MgAl_2O_4 , $(\text{Fe},\text{Ni},\text{Mn})\text{Al}_2\text{O}_4$, and NiFe_2O_4 . To some extent, these materials can be considered to be crystalline combinations of the individual metal oxides.

Certainly, many nonoxide ceramics are known, but most of them have serious limitations for the present purposes. For instance, covalently bonded ceramics—for example, silicon carbide (SiC) and silicon nitride (Si_3N_4)—are generally difficult to densify by pressureless sintering, and high pressures and temperatures are required to densify them by hot pressing [73]. Other nonoxides, such as alkali halides and similarly ionic materials, have aqueous solubility limits that are too high for the purposes of waste disposal. Of course, some nonoxide ceramics do not suffer from these or related waste-disposal limitations. Notable examples are provided by the gypsum-based materials and sulfur-polymer cement that were described earlier (Sects. 3.1.2 and 3.1.3). The first is based on an alkaline earth sulfate, and the other is a partially cross-linked, covalently bonded matrix. Nonoxide ceramics are not otherwise considered in the evaluation of candidate alternative final waste forms.

A variety of techniques is available for the fabrication of ceramic matrices [48,55,64]. Probably, the more relevant ones for final-waste-form applications are those for which powder processing procedures are used to form the component and sintering and hot-pressing methods are used to densify it and to tailor the microstructure. Some of the basic concepts that underpin the use of ceramic powders and the production of a dense, cohesive ceramic matrix with desired waste-form properties are given in Table XIII.

Raw Materials or Starting Components. Raw materials for the production of ceramics include crude materials from natural deposits, refined industrial minerals that have been beneficiated in order to remove impurities, and industrial inorganic chemicals that have undergone extensive chemical processing and

refinement in order to maximize chemical purity and to optimize physical properties [64,66,73]. Examples of the group of crude materials include clays (e.g., bentonite) and crude bauxite, which is an ore that contains nonhydrous alumina. Refined minerals, the sources for most industrial ceramics, include materials such as talc, which is a magnesium silicate described earlier and whose composition is $\text{Mg}_3(\text{SiO}_3)_2(\text{OH})_2$; bentonite and kaolin clays; rutile (t-TiO_2); silica (SiO_2); and dolomite, a double carbonate with the formula $\text{CaMg}(\text{CO}_3)_2$. Relevant industrial inorganic chemicals for the present purposes include solid single-metal oxides and solid multiple-metal oxides. Alumina (Al_2O_3), zirconia (ZrO_2), and magnesia (MgO) represent some of the families of single-metal oxides; spinel (MgAl_2O_4), cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), iron aluminum spinel (FeAl_2O_4), and mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) belong to some of the families of the more compositionally complex oxide materials.

Relevant inorganic nonoxide chemicals that can be used to fabricate ceramic matrices include salts that can react to yield, directly or via calcination of intermediate products, the oxides just indicated [52,56,63,65]. Oxalates, acetates, chlorides, nitrates, hydroxides, and carbonates typify such materials.

The metal alkoxides are an interesting group of nonoxide chemicals that can be used to prepare oxide ceramics [177]. These chemicals are a subset of the organometallic compounds described earlier in Sect. 3.4, but for which the R-group in compound (XXXVI) is a linear or branched alkane hydrocarbon ($-\text{C}_m\text{H}_{2m+1}$). Common compounds in this family are the metal ethoxides ($m = 2$), isopropoxides ($m = 3$), and tertiary butoxides ($m = 4$) [177]. Single-metal alkoxides are usually used in this regard, but mixtures of different metal alkoxides, in the desired stoichiometric ratio, can be easily prepared, hydrolyzed, and copolymerized to yield ceramics of complex composition [56,57,65].

The varieties of the chemical constituents available, the compositions that can be prepared, and the microstructures and properties that can be tailored are certainly broad. Hence, the technical selection of the appropriate starting materials depends on the ultimate compositions desired and the requirements demanded during processing and those for the final specimens.

Chemistry and Physics of Process. Important fabrication processes for ceramics are pressing, plastic forming, casting, and polymerization [48,55,61,64]. They are also the most viable ones for the preparation of intermediate specimens that will be sintered or hot pressed in order to make monolithic final-

waste-form pieces. Granulation techniques are suitable for preparing ceramic waste forms that ultimately are not monoliths (e.g., powders and capsules) after thermal treatment. These methods include the direct granulation of powders by compaction, extrusion, and pelletizing and the spray drying of slurries in order to make spherical granules [64,67].

Regarding monolithic ceramic waste forms, dry pressing can be used to make relatively dense products. Briquetted materials can be produced by roll compaction, a process that is related to dry pressing [64].

Plastic-forming processes include extrusion and injection molding, among other fabrication techniques [55,64,69,70,73,75]. The feed material for plastic forming is a low-viscosity liquid that contains a polymer binder with medium- to high-molecular-weight or colloidal particles. Alternatively, the feed may consist of a thermoplastic or thermosetting polymer resin. Important processing variables include the types and amounts of plasticizer and lubricant additives, the particle size distribution, the temperature, and the degree to which de-airing is accomplished [73,180].

Relevant casting modes include those resembling slip casting, pressure casting, and vacuum casting [64,73]. In slip casting, a slurry or suspension of ceramic powders is poured into a porous mold, and the cast piece is formed by filtration, which is driven by capillary suction on the mold. Generally, the properties of the slurry must be controlled in order to ensure a complete breakdown of physical agglomerates [64,83,88]. A balance between the particulate gelation rate and the casting rate must be established; otherwise, the properties (viz., density and strength) of the cast specimen worsen. Pressure and vacuum castings are performed using filtration arrangements, in which pressure is applied to the fluid side of the filter or a vacuum is established on the filtrate side of the filter, respectively.

Polymerization techniques emphasize sol-gel processing, such that monolithic pieces are made directly, bypassing the production of powders [65,73]. Gels or gelatinous solids that are similar to those discussed in the section emphasizing glass-ceramics (Sect. 3.4) are prepared using polymerization processes. Methods based on both metal salts and metal alkoxides are common [65]. The feature of these processes that distinguishes them from the foregoing ceramic processing approaches is that the balance between the hydrolysis stage and the subsequent condensation polymerization stages must be appropriately adjusted: that is, for materials derived from metal alkoxides, residual organic groups in the product may lead to

evolution of gases during thermal treatments. For materials derived from metal salts, residual anions can usually be washed out or removed via ion-exchange procedures.

Of course, sol-gel methods can be used to prepare powders, as indicated in the preceding description of ceramic raw materials and starting components. After the powders are calcined, these powders may be further processed using the techniques just mentioned [68].

Following the preparation of a ceramic component via pressing, plastic-forming, casting, or polymerization processes, it must be dried and thermally treated [55,64,73]. Drying may be carried out using conduction and convection ovens, with or without the application of a vacuum. The relative humidity or the partial pressure of the solvent (if it is nonaqueous) may need to be controlled if deleterious defects (e.g., cracks and nonuniform shrinkage that will negatively affect the success with which sintering and densification are accomplished) occur when the drying rate is too high [58,73,180]. Recent developments [73] permit the use of microwave ovens, supercritical drying, and freeze drying in order to remove the solvent.

The final generic step in the fabrication of ceramics that is discussed here consists of sintering and densification [48,49,50,51,54,64,65,73,180]. The thermal treatment that encompasses these processes involves three general stages. The formation of grain boundaries or a glassy matrix that causes the particulates to join together occurs in the first stage. These phenomena are followed in the second stage by a great reduction in the size of pores and the increase in the grain size. The transition from interconnected pores (i.e., remnants of the packing of powder in the presintered specimen) to closed pores establishes the onset of the third stage of sintering. The thermal treatment must be adjusted in order to approach full densification.

Common Variants. Hot pressing [71,72] is the principal variant that is described here. It normally promotes densification at a temperature that is approximately half the absolute melting temperature of the material to be sintered [73]. This technique uses both thermal and mechanical driving forces in order to achieve densification. Typically, billets can be made via this route. Hot pressing is useful when trying to sinter and to densify covalently bonded ceramics; in this case, a sintering aid, which may be an oxide with a low melting point, can be added in order to promote liquid-phase sintering

[48,49,50,51,54,64,65,73,180]. These additives may be expended in the process, or they may foster the formation of intergranular glassy phases. Hot pressing may also be used, of course, to treat oxide ceramics.

Thermal treatments may be tailored to promote sintering and densification under a controlled atmosphere. Commonly, this regulation involves the adjustment of the relative humidity and the partial pressure of oxygen or the maintenance of an inert atmosphere. Although the objectives in these cases vary, they are frequently to ensure that metal ions with variable valence within the ceramic are in the desired valence state, to ensure that volatile ceramic constituents do not volatilize (e.g., Cs^+), or to promote reactive sintering [54,73,180].

Properties. The ceramics that are emphasized in this section contain mineral-like phases. They are crystalline, inorganic nonmetallic materials.

Two fundamental approaches have been developed in order to shape ceramics. One is the use of fine ceramic powders that are mixed with a liquid, binder, or lubricant; this mixture exhibits overall rheological properties that permit shaping. Shaping can be accomplished by a variety of techniques that have been summarized earlier in this section. The second fundamental approach is to melt the material, and shaping is accomplished during the cooling and solidification stages. This approach is the one that is typically used in order to make glasses. However, it can also be used to make ceramics [54,55].

The raw materials and their preparation are the most critical factors that affect the forming and firing processes. Particle size and particle size distribution are of special importance. They set the limitations on the packing density that is obtained upon consolidation into a shape and are the ultimate driving forces for densification and sintering. The intimate mixing of the various powders, processing aids, and sintering aids is also critical in achieving the desired properties during the processing and firing stages. Clearly, the degree of mixing and the homogeneity in the prefired component are central to the attainment of uniform microstructure and reliable properties in the sintered component.

After drying (if wet processing such as casting is used) or after pressing (if dry processing techniques are followed), the ceramic prefired component is fired at elevated temperatures. Usually, the firing

temperature is in the range 700 to 1800°C. The composition determines the best temperature and whether or not thermal cycling is required. The mobility of solid constituents, such as molecules and atoms, may be enhanced by the presence of a high-temperature liquid-phase sintering aid. These additives can help to increase the densification rate (i.e., the rate at which pores are removed from the heated specimen), the tendency for grain boundaries to be established, and the rate of grain growth [54].

The chemical range of ceramics is very broad. Consequently, it is evident that the properties of ceramics are intimately linked to their composition. Also, in view of the facts that the thermal treatments of ceramic materials can vary considerably and that these treatments can be used to generate a multitude of thermodynamically stable or metastable phases, the properties of ceramic matrices sensitively depend, in most cases, on their microstructure. The specific critical microstructural features vary from system to system. Nonetheless, the arrangement of phases, including porosity, the relative amounts of each phase present, and the grain size and size distribution, shape, and orientation combine to provide the range of properties that the ceramic exhibits [54]. The development of the final microstructure depends on the sintering time, in addition to the parameters already identified.

Many properties sensitive to these factors are broad and include plastic deformation and elasticity; strength; and thermal, optical, electrical, dielectric, and magnetic behavior. Chemical reactivity and chemical durability are also set by factors other than composition; often the attack by chemical species is greater at grain boundaries than it is elsewhere. The mechanical properties of ceramics, especially their general brittleness, relate to the ability of the matrix to deform upon the application of thermal and mechanical forces [181]. The relaxation time for a ceramic underpins its general response to thermal and mechanical shocks in a manner akin to that described for organic matrices, glass, and glass-ceramics; see Sects. 3.2.1, 3.2.4, 3.2.5, 3.3, and 3.4, respectively.

3.6. Metallic Matrices

See Sect. 6.2.6 for a short description of the types of metallic matrices that are relevant to the assessment of waste-form technology, as addressed by the present report.

4. WASTES UNDER FFCA

4.1. Generic Categories

Seven generic categories of waste are specified in Table IV. The general properties and some representative examples of each category are also included in the table, and they underscore the broad breadth of wastes that may be encountered. The groups identified in this table are based on the chemical and physical hazards presented, as summarized in Table III.

In addition to their hazardous effects, the wastes in Table IV affect the various procedures to which they are subjected, such as treatment, solidification, and disposal. Thereby, the wastes directly influence the selection of the more suitable technologies by which they are processed [331]. This effect on the waste processing reflects the need to understand and to control both the hazardous and nonhazardous physicochemical properties of the waste (Table III). In this regard, the classification scheme in Table V reflects an attempt to group wastes generically according to the manner and extent to which the overall properties of the waste affect waste processing [331]. The members of the categories Aqueous Liquids, Organic Liquids, Organic Sludges and Solids, Inorganic Sludges and Solids, and Debris essentially match those in some of the categories in Table IV. However, those in the other categories given in Table V do not have analogous groups in Table IV. This lack of correspondence is not surprising in view of the fact that the categories in Table IV are based on the hazardous and physical properties, whereas those in Table V emphasize the practical differences for waste processing.

4.2. Specific Categories for the DDT&E Program

The quantities of stored wastes in the groups listed in Table V and those that are of particular concern for the DDT&E Program are tabulated in Table VI. This compilation reflects the inventory status, as of December 1993, and it summarizes the 1478 waste streams that are presently stored at 50 sites distributed over 22 states [331,332,336,335]. Approximately 40 vol % of the total quantity of waste that is presently stored is treatable via existing technologies.

The remainder demands that either modifications to existing waste-form technology be made or that new waste-form technologies be developed. Of the types of waste included in Table VI, the three most prevalent are aqueous liquids, inorganic solids, and debris.

Each type of waste listed in Table VI and newly added ones that pertain to the DDT&E Program must be successfully treated for disposal under the FFCA and related legislation. Consequently, a concise description of their definition and properties [331,333] is central to accomplishing this task. Moreover, the appropriate assessment of the candidate alternative waste-form technologies identified in Sect. 3 must consider the nature of the wastes themselves. In the absence of detailed chemical and physical analyses, the separate sets of waste characteristics and the effects on waste processing are addressed here in generic fashion. The waste properties that directly pertain to the performance criteria which are currently regulated, as described in Sect. 3.2, are taken into account. Specific waste-oriented concepts are developed where they are deemed to be warranted.

Aqueous Liquids. This category consists of those wastes that are primarily water and that contain less than 35 to 40 wt % settled and suspended solids. The aqueous liquids may contain organic carbon, but its total concentration must be less than 1 wt %. Importantly, these liquid systems may be further classified under RCRA as wastewater or nonwastewater.

Lab packs that contain aqueous liquids do not belong to this group. They are a subgroup within the category lab packs.

Organic Liquids. This category consists of those wastes that are liquid materials and are primarily hydrocarbons, such as petroleum distillates. They include slurries with a total organic carbon content that exceeds 1 wt %, and they have less than 35 to 40 wt % suspended and settled solids. Solvents are the primary type of organic liquids. The liquid wastes in this category may or may not be the hazardous component of concern.

Lab packs that contain organic liquids are not in this group. They comprise a subgroup within the category lab packs.

Organic Sludges and Solids. This category consists of solid or semisolid materials (i.e., other than debris¹⁸) that are mostly organic. Highly viscous liquids and sludges that are mixtures of liquids and solids are two common examples of the semisolid materials in this category. The wastes in this category

¹⁸Materials containing more than 50 wt % debris are classified as heterogeneous debris.

are generally homogeneous uniform materials with uniform composition. Examples include sludge from biological wastewater treatment plants, activated carbon, and organic resins.

Organic materials that contain less than 50 wt % belong to the present category, but those with more than 50 wt % debris are classified as debris.

Inorganic Sludges and Solids. This category consists of solid or semisolid materials (i.e., other than soil and debris) that are mostly inorganic. Mineralogical materials are also included in this category. The wastes in this category are generally homogeneous. Representatives include sludge from chemical wastewater treatment plants and dusts from air pollution control devices.

Wastes that have already been mixed with cement (i.e., cemented solids) are not included in this category. They require special handling and treatments. Hence, they belong to another category that consists, in part, of homogenous inorganic solids. Also, inorganic materials with more than 50 wt % debris are classified as debris, whereas those with less debris belong to the present category, inorganic sludges and solids.

Soils. This category consists of contaminated soils. The contamination derives from hazardous or radioactive materials. Mixtures of soil and debris with less than 50 wt % debris are in this category.

Mixtures that contain 50 wt % or more are not in the present category. They belong to the debris category. Similarly, contaminants that are stored in waste containers, rather than located in situ in soils, also require unique handling and treatments and, hence, belong to another category.

Debris. This category consists of wastes that are manufactured objects, plant and animal matter, and natural and geological (e.g., boulders and cobbles) solid materials. A restriction for debris waste is that the unit or particle size must exceed 60 mm (i.e., 2.5 in.) [363]. Mixtures of debris and nondebris materials (e.g., soils and sludges) are included in this category if the volume of the mixture is primarily comprised of debris. Debris is further categorized as organic and inorganic debris. Common examples of organic debris are discarded paper and plastic products, wood, and fabric materials, such as certain rags and clothing; examples of inorganic debris are metallic and ceramic construction materials, metal turnings, and glass.

Lastly, waste materials for which specific treatment standards are set [348], such as lead acid batteries, and process residuals, such as smelter slag and incinerator ash, are not classified as debris according to the Environmental Protection Agency (EPA) [336]. Debris composed of both organic and inorganic materials is generally classified as heterogeneous debris.

Lab Packs. This category consists of unique wastes. Generally, they include relatively small quantities of widely varied laboratory chemicals and discarded laboratory equipment.

Reactive and Dangerous Wastes. This category consists of wastes that can pose an acute physical hazard. Notable examples include reactive metals, explosives, and compressed gases. Sodium, other alkaline earth metals and their alloys, and various metal fines (e.g., those of aluminum, uranium, and zirconium) typify the reactive metals.

Wastes that contain reactive contaminants (e.g., various cyanide compounds) are not in this group. However, if the overall waste matrix is itself reactive, the system is classified as reactive and dangerous waste.

Inherently Hazardous Wastes. This category contains wastes whose matrix or primary components are toxic or hazardous. Common examples are liquid mercury, elemental lead, beryllium dust, and batteries (e.g., lead acid, cadmium, and other batteries). Elemental lead wastes include surface-contaminated lead. Bricks, counterweights, shipping casks, and other shielding materials typify the surface-contaminated lead materials. Activated lead from accelerators or other neutron sources is also in this category.

Multiple Wastes. This category groups those waste mixtures that are composed of materials that would conform to the requirements of more than one of the previously described categories. Hence, these mixtures may require sorting and separation prior to treatment. After such a procedure, the isolated wastes can be classified, grouped, and treated according to their respective waste categories.

Other Wastes. This category consists of those wastes that are not readily eligible to be classified as belonging to any of the previously described categories. Generally, the physical and chemical properties of these wastes are insufficiently known, and they need to be further characterized. In view of the fact that radioactive wastes do not constitute a separate category under the FFCA, they may appear in any

of the previously described groups, according to their nonradioactive hazardous properties. Combinations of low-level radioactive and hazardous waste components are classified as mixed wastes.

5. THE WASTE-MATRIX SYSTEM

The waste and the waste-form matrix compose the total system. The concept that it is this combined system which must be evaluated is often stated, but it appears not to be fully appreciated. Together, the composition of the waste and the microstructure of the combined system determine the properties exhibited by the waste-matrix system. Furthermore, it is evident that the composition and the physical state of the waste in the solidified (i.e., immobilized, originally hazardous component) are two integral features, among many, that contribute to the overall microstructure of the final system. Accordingly, these waste properties cannot be considered out of the context of the overall system. Having recognized that the nature of the incorporated waste is critical to the behavior of the total system, irrespective of the relative degrees of stabilization and encapsulation, we arrive at the inescapable conclusion that the degree of success with which the regulatory requirements are ultimately met is also set by the microstructure of the final waste-matrix system.

The preceding sections, Sects. 3 and 4, when considered in toto, demonstrate that an explicit statement of a new operating paradigm is useful, if not needed, regarding the perceptions of a candidate matrix and its viability and suitability as a final waste form. The relationships among (1) the chemistry (i.e., the composition and reactivity), (2) the processing history, (3) the microstructure of the combined, fabricated system, and (4) the properties of this final system demand that these aspects constitute a tetrad that governs waste-matrix behavior. Moreover, none of these aspects can be considered and altered independently of the others without introducing two detrimental consequences: a biased assessment of candidate (alternative) waste forms and error-prone predictions of their performance. The severity of the bias and the magnitude of the error depend, of course, on the sensitivity of the combined waste-matrix system to the concepts taken out of context and the altered parameters.

Therefore, it is again evident that the microstructure of the final-waste-form component is the key to the tailoring of its properties, including its ultimate ability to meet the regulatory and other desirable criteria. Important manifestations of this relationship and the related foundational concepts are often expressed as two common observations regarding waste stabilization and waste encapsulation. The first is that the ability of chemically stabilized waste species to migrate out of the host matrix generally differs from that of encapsulated waste under the same external conditions, and the second is that the degrees of

subdivision and homogeneity with which the waste is encapsulated in a host matrix contribute to the ability of that waste to be liberated or to migrate out.

In turn, the microstructure depends on two physicochemical factors, namely, the composition and the processing scheme used to fabricate the waste-matrix system. Alternatively, the microstructural features are, in essence, the manifestations of the overall composition, which derives from the waste and the matrix precursors, and the processing conditions that the combined system experiences.

Two examples of this principle are provided by a familiar waste-form technology, hydraulic portland cement; see Sect. 3.1.1 for a description of this material. The first example is that the processing of cement is sensitive to the presence of gypsum. The formation of acicular ettringite is enhanced when this additive is present. In turn, these needle-like grains of ettringite greatly affect the rheological properties of the cement system, and the changes in these properties are macroscopically detected as changes in the setting process and the workability of the cement. The second example is that the relative amount of alumina (Al_2O_3) in cement can control the resistance of the cement to corrosive attack by sulfate species [24,27,41,390]. Ordinary portland cement is easily attacked by sulfate species, such as those found in natural and polluted waters [41]. This attack results in a loss of strength, cracking, and, ultimately, disintegration of the cement. One reason for this effect is that anionic sulfate species react with the portlandite and CH phases described earlier to produce ettringite, which as it grows stresses the cement to expand and, eventually, to crack. High amounts of Al_2O_3 can be incorporated into the cement in such a manner (i.e., by altering the processing scheme) that the amount of CH produced by Reactions (1) and (2) is significantly reduced, if not eliminated [41] and, concomitantly, the average size of pores is reduced. This reduction in pore size increases the difficulty with which sulfate species can penetrate the cement. Secondly, the pores that are produced probably contain gelatinous alumina [41], which is less reactive toward soluble sulfate species than is the CH. These effects derive from changes in the selection of starting materials and, of course, the requisite changes in processing needed to incorporate more Al_2O_3 into the cement formulation. These changes combine to alter the microstructure that develops during the hydrolysis, setting, and hardening stages. The altered microstructure provides, in turn, an increased corrosion resistance and, thereby, benefits both the strength and crack-resistance properties that accompany it.

These two examples demonstrate important features. First, both the processing and the microstructure can be tailored by adjusting the chemistry of the system. Second, changes in chemistry nearly always require changes in processing. Third, the integrated model described earlier is useful for interpreting observations, designing the microstructure of a waste form, and regulating the properties that the system displays.

The paradigm provides a context within which the various wastes described in Table VI and the different families of candidate host matrices summarized in Table VII can be discussed. Moreover, the recognition that the total system subject to disposal comprises both the waste and the matrix resides at the core of this approach. For example, the wastes can be compared, based not only on their composition and their properties, but also on their effects on the microstructure of the overall waste-matrix composite system. This approach leads to an appreciation of the important features, and it suggests routes by which waste can be incorporated into the matrix. In optimized cases, this latter development would lead to chemical stabilization. Lastly, the paradigm and the concept of the overall waste-matrix system can be similarly used to tailor the fabrication stages. Then, the microstructural features that would most benefit performance criteria can be realized. These and related issues are discussed in Sect. 6.

6. COMPARISONS

6.1. Types of Wastes in the DDT&E Program

The general types of wastes of concern within the DDT&E Program are listed in Table VI. The three most prevalent types of wastes affected by RCRA [360,361,362,363,365], LDR [364], and FFCA [347,348], as described earlier in Sect. 4, are aqueous liquids, inorganic sludges and solids, and debris. Together, the wastes in these categories constitute more than 91 vol % of the total waste to be treated for disposal.

The assessment of the alternative candidate waste forms (Sect. 3) must take these and the other types of waste into account. Hence, a brief discussion of the problems encountered or likely to be encountered with members of the generic groups in Table V is desirable and aids the assessment process. Important issues that pertain to the solidification of the three most prevalent types of waste follow. A perspective that underscores the contributions of the waste to the regulatory performance of a waste-matrix system is used. This perspective emphasizes the effects on the solidification stages in the processing of the waste and the waste-matrix microstructure that primarily derive from the waste. Following the general comments on the problems associated with the generic wastes, particularly problematic wastes are described. The operating paradigm presented in Sect. 5 is shown here to facilitate the elucidation of the key waste-derived factors. Its use specifically clarifies the roles that the interrelationships among the chemistry of the waste-matrix mixture, the processing of this system, the development of the ultimate microstructure in the solidified specimen, and the properties of this final system may have in establishing the performance under specified conditions.

6.1.1. Generic Categories

Aqueous Liquids. The aqueous wastes consist primarily of water and contain less than 1 wt % organic carbon; see Tables IV and V and Sect. 4. The maximum solids content in these systems is on the order of 35 to 40 wt %; that is, the waste must be pumpable. According to the data in Table VI, this type of waste represents approximately 45 vol % of the total waste to be treated for disposal in the DDT&E Program.

Two important problems that are encountered with these wastes relate to the fact that the salt in them can degrade the performance of organic thermoplastic and cement-based waste forms. The thermoplastics are susceptible to the osmotic swelling induced by the salt. The cement-based forms and glasses also may be sensitive to the stresses generated when the dissolved salt reacts with constituents in the intermediate and final stages of processing.

The suitability of other waste forms can also be degraded by aqueous liquids. Some of these liquids contain salts and contaminants that present problems of volatilization, acid gas, and off-gases for high-temperature operations. Inorganic waste forms can be susceptible to these problems, including vitrified (glass) materials, devitrified (glass-ceramic) materials, and ceramics. The low solubility in glass of some of the solutes in aqueous liquid wastes can limit the usefulness of vitrified matrices and, in general, the vitrification process. Finally, strongly caustic solutions can attack sulfur-polymer cement, rendering it unsuitable for such aqueous liquids.

Organic Liquids. The constituents of these wastes are primarily hydrocarbons, such as petroleum distillates. When solidification is attempted with cement-based systems, these wastes can interfere with the setting process. The waste species can blind the surfaces of the various powders in the cement mixture (clinker) via adsorption-desorption processes, similar to the action of organic retarders [41,370]. Under these circumstances, the hydration of the surfaces is incomplete. In fact, in the worst cases, these wastes can prevent the formation of the final waste form altogether [389,397.]

Another problem posed by these wastes is that they can act as solvents that attack organic matrices. These wastes can dissolve parts of the bitumen structure. In fact, the high solubility of aromatic hydrocarbons and asphaltenes, major constituents of the bitumens used for solidification of hazardous waste [9,10,376,378] in liquid alkanes, is the fundamental principle that underpins the accepted analytical procedures used to fractionate bitumen [9,10]. This phenomenon may weaken the bitumen matrix, and the degradation would worsen with extended age. This reduced resistance to chemical attack and its related effects (viz., softening, among others) would also detract from the usefulness of bitumen in a variety of waste management phases [378]. These wastes can also present similar problems for other organic thermoplastics, such as polyethylene and poly(vinyl chloride) [385]. In related fashion, the relatively high solubility of sulfur in aromatic organic liquids, such as benzene, toluene, phenol,

pyridine,¹⁹ quinoline, *m*-xylene, and *p*-xylene [297], suggests that these materials, if present in the waste, can attack sulfur-polymer cement.

A third problem that these wastes can foster relates to the temperature at which the waste form is processed. The hazardous constituents of these wastes can become volatile at ambient and slightly elevated temperatures. Typically, they do not decompose at these temperatures because temperatures on the order, say, of 400 to 600°C or higher may be needed for decomposition. Unfortunately, this range of temperatures overlaps with that needed to fabricate most organic matrices [213,220,222]. Consequently, the loss of waste species can occur during processing stages. Additionally, the organic waste, especially solvents in it, can add to the flammability of the waste-matrix system under conditions that otherwise might not be a problem [498].

Inorganic Sludges and Solids. Inorganic sludges and solids comprise approximately 33 vol % of the total waste to be treated for disposal in the DDT&E Program. This volume makes this waste category the second most voluminous of those in Table IV. Solids of mineral character may be either wet or dry and can present problems that resemble those identified in the following discussion for problematic soils.

Soils. Contaminated soils, when placed into a waste-form processing scheme, have the potential of releasing the hazardous components and nonhazardous constituents to the bulk of the processed system. Various mechanisms exist. As examples, the soluble species, such as some chromates, may occur by dissolution, whereas other species that are volatile or semivolatile are released by vaporization, as can be the case for mercury. Certainly, the release of insoluble species can accompany comminution processes. Irrespective of the combination of mechanisms that may operate, these components can detrimentally affect the waste-form matrix in the fashions already indicated. Then, the chemical and physical properties of the species in the released state dictate the range of potential problems.

Soil itself can present problems during processing. These may be associated with the granularity of the particulates. Abrasion of equipment may be important. For instance, it may limit the usefulness of processing schemes and, therefore, the waste-form matrix. Soil constituents can also detrimentally

¹⁹Although it is not a benzene (aryl) ring, the pyridine ring possesses unsaturation that resembles that of the other compounds listed.

introduce network-breaking minerals or related species (e.g., alkali metal oxides) into a vitrification system. This behavior would reduce the durability of the glass by inhibiting the establishment of the three-dimensional network microstructure that underpins the properties of the glass. The impact of such behavior on the leaching process and the chemical resistance of the glass has been reported in connection with the vitrification of nuclear waste [455]. These species may also degrade the resistance of the glass to corrosion by acidic solutions [452]. The oxides that are responsible for these reductions in performance are common constituents in soil [85]. Inversely, soils can introduce network-forming silicates into a ceramic process that can generate a glassy phase in the final product. This glassy phase can then contribute to a reduced chemical durability, as compared with that found for ceramic matrices without glassy phases [401,402,412]. In view of the facts that (1) sintering aids, some of which are siliceous, may be needed in order to densify ceramic matrices [413], (2) amorphous silicate glassy phases have been found in otherwise crystalline ceramic waste forms [406,410], and (3) soils contain many siliceous fundamental structural units [81,85], it is anticipated that soils could contribute to the establishment of less-than-optimal microstructures. Furthermore, owing to the fact that the performance of ceramic matrices is intimately linked to their microstructures [411,412], it is further evident that too much glassy phase in the ceramic waste-form matrix will permit the matrix to be corroded by agents that typically corrode glass. This corrosion would lead, in turn, to poorer waste matrix performance.

Debris. The wastes in this category represent approximately 13 vol % of the total waste to be treated for disposal in the DDT&E Program, according to Table VI. The category consists of materials that span a broad range of properties. Organic, inorganic, and metal pieces, in addition to ashes, are members of this group.

One important problem that is encountered with these wastes relates to the fact that some metals can be oxidized to more thermodynamically stable forms. This development can present special problems for some types of waste forms. As examples, iron and aluminum, which may be present in the form of thin sheets and turnings, are among the most prevalent problematic metal wastes [336]. They are particularly troublesome when the shapes of debris objects have a high surface-to-mass ratio. Also, in view of the fact that the oxidation of these metals can be made easier by the waste form, the waste form itself may exacerbate an already troublesome situation.

One example demonstrates this state of affairs for debris. Consider iron debris that is incorporated into hydraulic cement. The water in the cement mixture may help to constitute a conduit for electrical current, and a highly localized electrochemical cell may then be established by which the metal can be oxidized, if the normal cement passivation of iron is overcome by the conditions of lower pH that would be generated by carbonation or penetration of the matrix by aggressive salts species, such as chloride ions. When this scenario occurs, hematite (Fe_2O_3) forms. It is stable, and, as this material grows, it occupies a larger volume than that lost by the chemical reactions. The net expansion is on the order of 300 vol %. The effects of this expansion on the cement waste form resemble those found for the rebar-reinforced concrete roads and bridges in the northeastern United States; after having been salted in winter, these structures harden, crumble, and spall. Thus, iron debris can lead to similar effects in cement-based waste forms. Other metals, notably aluminum, beryllium, and uranium, may behave likewise.

Lab Packs. These wastes, based on the information supplied for heterogeneous wastes in Table IV and the descriptions given earlier in Sect. 4.2, may be understood to be containers that are filled, even partially, with hazardous wastes. This description leads to the realization that problems with these wastes arise when the lab packs are broken. This release of hazardous wastes, irrespective of whether or not it is accidental, then creates situations resembling those already described. The release of aqueous liquids, organic liquids, or members of the other groups via such a mechanism can generate the same problems that the hazardous wastes would in the absence of the containers. Metallic, siliceous, and ceramic (i.e., inorganic with mineral-like phases) container materials may require more complicated processing schemes than those solely predicated on the properties of the hazardous wastes. Certainly, the container materials may also exacerbate the chemical problems posed by the hazardous waste components. Thereby, the solidification process and the development of the microstructure in the waste-matrix system may be inhibited or otherwise detrimentally affected.

Reactive and Dangerous. Reactive metals and metal fines in this group can affect the processing of the waste matrix in much the same manner as that already described for debris, except that the reactions may be faster. If pyrophoric, these wastes may demand special processing.

Inherently Hazardous Wastes. The problems that this group of wastes present are similarly understood as special cases of the previously described problematic wastes. Elemental metals (e.g., lead, beryllium, and mercury) may exhibit influences on the processing of the waste and the microstructure of the

waste-matrix composite system, as previously discussed in this section. Additionally, liquid mercury may be released during processing at elevated temperatures.

Multiple Wastes. The composition of these wastes varies considerably. Upon the application of separation procedures designed to segregate the constituents into groups of wastes with similar hazardous, chemical, and physical properties, the problems associated with each of these subgroups resemble those already described for the individual groups. An added concern with multiple wastes is that chemical reactions may occur when wastes from different generic categories are present together in the mixture. The problems generated by the products of these reactions depend on which of the preceding categories are represented during and at the end of the reaction sequence.

Other Wastes. These wastes are largely not characterized; see Table V. Upon the receipt of relevant data, they can be classified into the other groups. The problems with their solidification and disposal are then similar to those for the other wastes that are similarly classified.

6.1.2. Problematic Wastes: Prevalent Wet and Dry Wastes

Some wastes present special problems. Three such classes are aqueous liquids, inorganic sludges, and ashes. These wastes may be regrouped, in a somewhat more simplistic manner, as wet (aqueous) wastes and dry (inorganic) wastes. This classification differs from that adopted throughout the other sections of this report. Still, it has the advantage of facilitating the assessment of alternative waste forms, especially when combined with the key issues discussed in Sect. 5.

Wet (Aqueous) Wastes. These wastes, viz., aqueous liquids and inorganic sludges, comprise approximately 70 vol % of the wastes stored at DOE facilities [331,332] and affected by the FFCA; see Table VI. Experience suggests [336] the usefulness of further classifying these wastes. Appropriate subcategories are (1) high-solubility saline systems, (2) low-solubility salt systems, and (3) special wet systems.

The wastes in the first subcategory, high-solubility saline systems, contain salts whose total concentration exceeds $\sim 5 \text{ mol dm}^{-3}$. The osmotic pressure generated by such highly saline systems can be very high when they are incorporated in a waste-form matrix. This situation is especially acute when

the matrix is an organic thermoplastic [377]. The excess pressure can induce swelling in such cases. Moreover, salts that have a very high aqueous solubility (e.g., sodium nitrate) reduce the vapor pressure of water above the waste solution. When this reduction occurs in the presence of a hydrophobic organic thermoplastic that can concomitantly act as an impermeable membrane, swelling ensues. For example, the excess pressure generated by sodium nitrate in bitumen has been estimated slightly to exceed 30 MPa (i.e., 300 atm) [377].

Other thermoplastics can be subjected to the similar internal forces. The time required to observe such effects (swelling) depends on the chemical composition and the microstructure of the waste-matrix combination. Consequently, short-term regulatory-based tests may not detect the swelling or other osmotically derived effects for some matrices, whereas they do for others. Clearly, in the absence of appropriate investigations, a candidate waste form must be able to withstand the internal stresses associated with the osmotic pressure, if it is to be considered suitable for wet, highly saline wastes.

High-solubility saline wastes can also lead to other problems. Water in wastes of high salinity can react with certain waste forms and, thereby, induce the precipitation of inorganic phases. If extensive, the subsequent growth of these phases lead, in turn, to nonosmotic expansion pressures. Inversely, such systems can be equivalently viewed as deficiencies or defects in the waste form: that is, the matrix would be discontinuous at the surfaces of these precipitated solids. The properties of the matrix would be correspondingly degraded by the presence of these inclusions.

Hydraulic cement (Sect. 3.1.1) is a good example of a waste form for which regions with incorporated and otherwise retained water of high salinity comprise defects in the microstructure. This matrix has a large thermodynamic tendency to hydrate alumina- and silica-based phases [41]. During the curing stage of the hydraulic cement, water is slowly removed chemically, and the dissolved salt, already at high concentration, is further concentrated. Specifically, it concentrates in the interior of the macropores that prominently comprise, in part, the cement microstructure. Eventually, the concentration of salt in the pore liquid may rise to supersaturation levels, and the precipitation of salt crystals ensues. These crystals, upon sufficient growth, exert forces on the cement matrix that may cause it to crack and to spall. In such cases, the chemical inertness of the salt may manifest itself in the apparent loss of cohesiveness in the waste-form matrix. This weakening effect has been observed with hydraulic cement [336].

The second subcategory of problematic wet (aqueous) wastes consists of wastes that contain salts of low aqueous solubility. The alkaline earth-based carbonates and hydroxides typify such salts because they are virtually insoluble in aqueous media. Hence, the group of problematic wastes addressed here includes the sludges that form during the alkaline precipitation of metals. Water-softening processes typically also generate sludges in which salts of low solubility reside. Clearly, if low-solubility sludges are combined with highly soluble salts, for instance, as might be done during waste processing, the osmotic pressure effects discussed earlier may result. Here, the low-solubility components will drive the precipitation of new phases that eventually affect the waste-form matrix with detrimental consequences.

It is noteworthy that wastes can be accommodated by the microstructure of some waste forms, if the relationships among the chemistry, the processing parameters, the development of microstructure, and the ultimate properties are taken into account. This approach may be driven by insight into these relationships or it may lead to practical improvements if the interrelationships are appreciated, though they may not be fully understood. An example that applies to each of these cases is the introduction of thermal processes in the processing scheme. Wastes that contain components with very low solubility limits can be thermally processed in order to reduce the volume of waste and, most importantly, to remove water that provides the medium in which the various reactions just described occur. Intermediate thermal processing stages may also be specially designed for some wastes in order to tailor the microstructure. However, just as critical, these stages may be designed with sufficient flexibility to permit the thermal treatment of wastes whose salinity is not characterized well. Such an approach presumes the interrelationships earlier.

The third subcategory, special wet systems, consists of wastes that contain chemical species that pose specific problems for certain waste forms. Soluble aluminum in the anionic aluminate form and soluble boron in the borate form are two representatives of this group when hydraulic cement waste forms are considered. The first species may induce rapid setting of the cement, whereas the second one may retard the setting process in this same type of waste-form matrix [399,400]. Furthermore, aluminate species may also react to form expansive minerals (e.g., ettringite) when in the presence of sulfate species. This phase can, in turn, induce swelling in cement-based matrices, in much the same mechanical manner cited earlier for precipitated inorganic phases in wastes of either very high salinity or of salts with very low solubility.

Generally, special problematic species, such as those just described, do not affect thermoplastics in this manner. Still, they can generate other detrimental effects in these matrices. As an example, consider encapsulated sodium sulfate crystals; they can retain large quantities of water, as waters of hydration. Although some of this water is removed during the thermal processing, an encapsulated sodium sulfate crystal will thermodynamically be driven to reabsorb water from its surroundings. This phenomenon results in an increased crystal size. As in the case explained earlier for insoluble salts, the expanding sodium sulfate crystal can exert enormous pressure on the surrounding matrix. In this waste-matrix system, sodium sulfate is insoluble. Ultimately, deep crevices may be observed in the host waste form.

Interestingly, the combination of swelling and cracking of the waste form that may occur in the case of thermoplastics is clearly the result of mechanical effects which are qualitatively similar to those just described for cement-based waste forms: that is, stresses on the matrix arise from the presence of an expanding inclusion. The specific conditions within the matrix that give rise to catastrophic failure differ, probably markedly, from those cited earlier for salts and other inorganic phases which are entrained in a predominantly inorganic, crystalline cement. The similarities and the differences between these two generic waste-matrix systems are included in the microstructural considerations within the operating paradigm.

Dry (Inorganic) Wastes. Ashes exemplify this group, being primarily inorganic materials, even though they may contain very low concentrations of carbon. They are generally composed of silicon oxides and aluminum oxides, in combination with trace elements. These dry inorganic wastes are the oxidized by-products of combustion processes that other wastes undergo. Examples include alumina and silica. For example, solids derived from alumina and silica are often very reactive in alkaline solution. As a consequence, they are good hydraulic reactants, in that they readily lead to some of the components in cement-based waste forms. For this reason, Class F fly ash from coal burning operations is an especially good extender and is used in order to minimize the amount of portland cement needed.

Such dry wastes may, however, present problems. They are extremely abrasive in extruded thermoplastic matrices (e.g., bitumen and polyethylene) when their concentration is high [366], and this abrasion can limit the waste loadings that are practical when ashes constitute part or all of the waste incorporated into organic thermoplastics. Moreover, this abrasion demands, in turn, energy-intensive mixing procedures in order to incorporate the particulates into extruded thermoplastic matrices [336].

Intolerable degrees of wear result, despite the fact that the thermoplastic may lubricate ash surfaces while encapsulating the particulates.

Problems can also arise during the incorporation of dry particulate wastes, such as ashes, into other thermoplastics that do not rely on extrusion processes. In fact, such behavior is not limited to organic matrices. The ability to process sulfur-polymer cement (Sect. 3.1.3) via melt processing techniques suffers from these effects too. Here, segregation of the waste may occur in the melt, and the degree to which it occurs depends on the specific processing techniques used to encapsulate the dry waste. In this waste-matrix system, however, the specific gravity of the dry inorganic particulate waste (e.g., ash) typically differs significantly from that of the molten sulfur. In severe cases when this occurs, the dry particulates float to the surface of the molten sulfur. This perturbation on the uniformity of the melt results in a gross inhomogeneity in the ultimate microstructure. Clearly, the waste-matrix microstructure in the solid derived from such a melt that is affected in this manner exhibits final properties quite different from those in which the dry waste is distributed uniformly, first in the melt and then in the solidified specimen.

6.2. Final Waste Forms

The generic potential waste-form matrices are varied regarding their chemistry, the processing requirements, and the treatments that waste must undergo in order to be incorporated into them. The complexities that the earlier sections described, the range of wastes that must be considered, and the composite nature of the overall system, comprised of the waste and the matrix, warrant a review of the generic matrices in a manner that their advantages and disadvantages are highlighted.

The review that follows helps to place the alternative matrices in a perspective that permits their uses as waste forms to be assessed. The behavior of each type of matrix containing specific wastes is emphasized for cases that have been adequately documented in the technical literature. For cases in which the behavior has not been documented, the behavior of each type of matrix that can be anticipated is summarized.

6.2.1. Inorganic Matrices

Three types of inorganic matrices are described in Sect. 3.1. They are cement-based materials, gypsum-based materials, and sulfur-polymer cement (SPC). The discussions in that section, the information in Tables VII and VIII, and the proprietary nature of many fundamental aspects of gypsum-based processes justify the emphasis placed here on cement-based and SPC matrices.

Cement-Based Materials (Grouts). The advantages of the cement-based waste forms relate to their technical feasibility (Sect. 3.1.1) and the time frame within which they can be implemented for the treatment of hazardous and mixed wastes. Commercial processes exist for their production, and they are the most widely used waste forms for hazardous, radioactive, and mixed wastes. The varied experiences with cement-based forms (e.g., grout, which is a mixture of portland cement and water that does not contain aggregates [359] but may contain admixtures in order to improve properties) document a proven track record. For these reasons, the Environmental Protection Agency (EPA) specified grout as the best demonstrated available technology (BDAT) for a few select wastes [354,363].

Additional advantages are that the raw materials or starting materials for cement-based forms are plentiful and inexpensive [23,30,40,41,46,151,390]. Dewatering and extensive drying stages are not needed. Importantly, these matrices are generally tolerant of chemical variations in the matrix chemistry and waste composition. If leaching characteristics must be improved, cement-based matrices can be treated, in some cases, with sealant in order to alter the leaching behavior and to achieve acceptable performance.

Some cement-based matrices, referred to as grouts [359], and related materials have a long history of acceptable performance as final waste forms for hazardous, radioactive, and mixed wastes [379,383,384, 385,388,398]. Much is known about this type of matrix and its ability to immobilize waste [392,393]. The abilities to inhibit and to reduce the capability of hazardous species to leach out of the waste-grout composite have been central features to the success of cement-based waste forms. Consequently, the leaching mechanisms have been emphasized in recent research, and various mechanisms by which hazardous species can be leached out of these materials have been proposed [392]. They involve at least one of the following phenomena: the solubilization of hazardous species and matrix constituents, the

solid-state transport of these hazardous species, the surface migration of weakly bound waste species, the diffusion of waste species in the pore liquid, and the chemical and biological attack of the matrix.

The identification and the understanding of the various leaching mechanisms, which operate in both the systems that are successfully formulated to immobilize the waste and those that are not, have required physicochemical and microstructural analyses [393,394], and the crystallography and morphology of prevalent phases have been found to be especially important. Also, the effects of the dynamic stages of processing on the final matrix properties have had to be understood and controlled [391]. The most successful applications resulted from the effective manipulation of the interrelationships among the grout composition, waste composition, processing history, and the establishment of specific microstructural features. In other words, the careful manipulations of the various components of the paradigm described earlier (Sect. 5) ensure the successes realized with cement-based waste forms. These manipulations of the waste-grout system were based on both traditional physicochemical data and advanced microscopic studies [275,381,383,384,385,388, 391,398]. Notably, many of the successful applications are based on the composition and properties of the waste, and recent research has confirmed the need to control the solid microstructure and the liquid composition [386,387].

Cement-based matrices possess some disadvantages that limit their use as waste forms. Relatively large amounts of cement are required to incorporate waste [383,384,385]. The viability of using these matrices may be sensitive to the internal and external pH conditions [45,393]. Mildly acidic environments can be problematic [366], and nitrogen-rich alkaline environments may lead to the production of ammonia gas. Consequently, the extensive pretreatment of the waste [399,400] and the use of high-cost additives may be needed in order to circumvent these problems [382,386,399,400]. Cracking and fracture phenomena, associated with the freeze-thaw cycles, can induce damage in otherwise acceptable cement-based waste forms. In such instances, the addition of attapulgite clay can improve the structural integrity of these waste forms [386].

Other problems derive from the incorporation of highly saline waste into the grout matrix [399,400]. In these cases, the problems relate to both the processing stages, particularly the setting behavior, and the stresses generated by inadequate control of the mineral-like crystallographic phases that precipitate within the grout pores. The processing problems resemble the behavioral aspects described earlier for waste-free systems (Sect. 3.1.1): that is, the formation of new phases with anisotropic morphology

affects the rheological behavior of the cement, and, thereby, the setting process. Inadequately formulated grout is susceptible to these stresses, established by the formation of expansive salt crystals, and, eventually, the overall immobilization performance degrades; the chemical and physical aspects of these effects were described earlier (Sect. 6.1.2).

Summarizing Comments. Cement-based waste forms, especially grouts, have proven successful in many waste solidification/stabilization (S/S) applications. Recent applications include those for mixed waste [337,389] and radioactive wastes [388,390,398]. These successes stem from the optimization of the interrelationships comprising the paradigm described earlier. Some of these successes have naturally occurred, based on the collective technical expertise developed after many years of empirically studying cement and concrete for the purposes of waste disposal and other operations. Nonetheless, much of the early research cited in Sect. 3.1.1 and in the present section relied on careful analyses of the compositional and microstructural features of the waste-free and waste-containing matrices.

When these were used to interpret the various types of processing behavior and the ultimate properties of the solid system, the range of uses for cement and grout was greatly expanded. This development presently continues in waste-related and other industries that make use of such systems.

Some of the problems cited earlier stem from the open porosity in the cement-based matrix. Other problematic manifestations of this and the closed porosity relate to the handling, storage, and burial aspects of disposal. Specifically, upon the incorporation of certain hazardous, radioactive, or mixed waste, the cement-based grout can occupy an unacceptably large bulk volume: that is, compared with the initial bulk volume, the volume of the overall waste-matrix composite system can be large, resulting in a significantly greater amount of material that must be treated for disposal. Porosity-related issues such as these can limit the implementation of grout technology for the purposes of waste disposal. This effect derives from the recognition of two important materials issues. First, the processing methods for many of the other waste forms (e.g., sulfur-polymer cement, organic thermosetting resins and thermoplastic polymers, glass, glass-ceramics, and ceramics) normally yield products whose densities approach their respective theoretical values. Second, these waste-containing matrices are not greatly porous, as the microstructural descriptions for the cited matrices, which permeate this report, note where relevant. Thus, the specific bulk volume of waste-containing grout-based specimens (based on waste

content) can be unacceptably high when alternative waste forms ensure less bulky items for handling, storage, and disposal.

Lastly, in view of the fact that cement-based grout is a baseline technology for the DDT&E Program, it is noteworthy at this point that this matrix is inadequate for all wastes [337]. Some important wastes leach too readily from grout. Examples include the losses created by the desorption of radionuclides [395] and the impermanent immobilization of volatile organic compounds by grout that contains limestone [397]. Furthermore, the incomplete chemical reactions (viz., hydrolysis) in grout can also lead to detrimental, time-dependent leaching behavior, and the hydration of grout can be critically inhibited or completely arrested under ambient conditions by some waste species (e.g., organics).

Gypsum-Based Materials. Although solidification processes based on the use of gypsum were developed for nuclear waste applications [385], their use appears not to have been extended to hazardous waste until very recently [390]. Many of these processes are proprietary [493]. Still, some details about this technology are available [385,390]. The Envirostone® process developed by U.S. Gypsum [493,494] and some aspects on the use of gypsum for purposes of solidification [487,488,489,490,491,492] are also documented. Unfortunately, little information is available from independent studies.

Nonetheless, some advantages have been identified for gypsum-based materials. Two are that the inorganic raw materials or starting components are widely available [487,488,489,490,491,492] and much of the chemistry and microstructural development that occurs within this family can be anticipated (Sect. 3.1.2). Additional advantages relate to the facts that little specialized equipment is needed, the chemistry is relatively well known, and dewatering is not needed because the hydration reaction consumes the available residual water in the waste. Additionally, the resistance to water can be significantly increased if a hydrophobic resin is incorporated into the matrix. Consequently, hazardous and radioactive wastes have been successfully solidified using gypsum-based matrices [487,488,489,490,491,492,493,494].

No major additives are needed for gypsum-based waste forms because they are self-cementitious [385]. These systems also set faster than the comparable cement and lime-based systems. They are stable and are not susceptible to biodegradation; flammability is not an issue with gypsum-based final waste forms.

In addition to the unattractive aspect of the requirement for a proprietary polymer [493] in these materials, three other important disadvantages exist for gypsum-based materials when used as waste forms. First, gypsum and other additives add to the weight of the overall waste-matrix system and, therefore, to the bulk of material to be transported and treated for disposal. Second, gypsum-fixed materials that are not coated may require specially designed landfills to address leaching problems [366]. Third, although this treatment generally encapsulates the waste, it typically does not provide chemical stabilization.

The use of these waste forms may be restricted to high-sulfate or high-sulfite sludges. Also, they generally exhibit leaching characteristics that resemble those for cement; this feature is apparently the result of the microstructural similarities between these waste forms. Gypsum-based matrices may also demand a calcination step [487], an energy-intensive process and one that can complicate the design of the overall process scheme.

Sulfur-Polymer Cement. Sulfur-polymer cement (SPC) primarily consists of sulfur and low concentrations of organic additives, typically totaling about 5 wt % [316]. These additives are unsaturated polyolefinic hydrocarbons (e.g., dicyclopentadiene and cyclopentadiene) [300,305,316] and glycols [304,316]. SPC requires melt processing techniques and can be formulated to contain low levels of concrete aggregate [315] and mica particulates [304], in addition to the organic additives. See Sect. 3.1.3 for further details.

A related structural material, sulfur concrete, resembles SPC, but its composition contains considerably more concrete aggregate, on the order of 63 wt % [305,315]. Whereas the sulfur in SPC constitutes most of the matrix, its role in the composite sulfur concrete is to bind the aggregate particulates [297,315]. Of these two forms of sulfur-containing matrices, SPC is emphasized herein and is the focus of ensuing discussions on sulfur-containing matrices as alternatives to grout and glass.

SPC has been found to possess beneficial properties, regarding its use as a final-waste-form matrix for hazardous, radioactive, and mixed wastes [519,520,521,522,526,527.] It has been found useful for the encapsulation of mixed waste ash, produced in secondary waste streams from the cleanup of vitrification off-gases [518]. Recent reviews [525,526] provide a range of details regarding these uses and the degrees of success for SPC at meeting various performance criteria. The beneficial properties of SPC derive from

those of sulfur, which is thermodynamically stable [290,296,302,304,305], mechanically durable [291,292,293,309, 310,311], tolerant toward extreme freeze-thaw cycling [289,293,315], and chemically resistant to corrosive environments [293,305,312,316].

Some of the processing aspects of SPC originate with the properties of elemental sulfur. Its melt is a thermoplastic fluid [287,296,297,316,525], as a result of the linear chains of sulfur rings; in this regard, it resembles the vinyl-based thermoplastic polymers. As the melt cools, the molten sulfur, partially cross-linked in the case of SPC, progresses through a liquid-to-solid transition. Consequently, the rapid hardening of SPC that has been frequently reported [525,526] is the result of the formation of a dense [519] solid microstructure that forms upon cooling. Furthermore, as was pointed out in Sect. 3.1.3, and reinforced in later sections (e.g., Sect. 3.2.5), small degrees of cross-linking can enhance the strength and hardness of thermoplastic materials. Hence, the limited cross-linking in SPC, which is achieved via the reactions between the polyolefinic additives and the sulfur, imparts a greater strength and hardness to the material, and this set of improved properties is evident early in the setting stage. Extensive cross-linking would transform it further toward being a thermosetting material. This approach seems to be unexplored.

The relative chemical inertness of SPC underpins the prevalent finding [519,520,521,522] that various waste species are encapsulated in SPC, rather than chemically stabilized in it. As a result, it can be anticipated that many diverse types of waste can be successfully incorporated into SPC. However, few have been examined with this perspective [525].

SPC also exhibits properties that are disadvantages in terms of its processing. The wastes need to be nearly fully dry prior to encapsulation in SPC [525]. Although water does not easily permeate SPC, owing to the hydrophobicity of sulfur (Sect. 3.1.1), water can present problems nonetheless. If present in sufficiently high concentration (viz., greater than approximately 1 wt %), liquid water can act as a local reservoir for electrolyte species in the encapsulated waste. Under these circumstances, the problematic situations that were described earlier for wet (aqueous) wastes (Sect. 6.1.2) can arise. The waste form can experience excessive stresses, attributable to osmotic forces, and swell in response. Such behavior has been reported for SPC [519,522,525]. Ultimately, the swelling can lead to cracks and fracture.

As noted earlier regarding the impact of some organic liquid wastes on SPC (Sect. 6.1), SPC is susceptible to attack by strong alkalis and aromatic organic liquids, such as those characteristic of some waste streams on the ORR. Some waste species are volatile at the temperatures typically used to process SPC. Additionally, hydrogen sulfide (H_2S) and other sulfur-containing gases can be generated during processing. These could constitute seriously problematic off-gases; as a consequence, secondary waste streams might be generated when SPC is used.

Summarizing Comments. Based on the discussions in Sect. 3.1, the information in Tables VII and VIII, and the fact that many of the fundamental aspects of gypsum-based processes are proprietary, cement-based materials and SPC matrices are emphasized here. The first is a baseline technology, and the second is an inorganic thermoplastic matrix that, although it has recently received much attention, must be regarded as representative of an encapsulation technology in need of further development for hazardous, radioactive, and mixed wastes.

6.2.2. Organic Matrices

Two major types of organic matrices are described in Sect. 3.2. These are thermosetting resins and thermoplastic polymers. Multiple members of each family are described. The discussion in that section and the information in Tables VII, IX, and X underscore the generic properties of each family, although specific chemical reactions and species were emphasized in order to develop a general description for these materials. While the microstructures of these materials differ considerably among the various families, they generally would favor the retention of waste species via encapsulation mechanisms, rather than by chemically stabilizing interactions.

Thermosetting Resins. Thermosets that are derived from urea and formaldehyde, epoxies, and unsaturated esters were described, respectively, in Sects. 3.2.1, 3.2.2, and 3.2.3. The discussions in those sections and the information in Tables VII and IX emphasize three important areas: the major condensation polymerizations for each type, the cross-linking reactions that generate the network structure that characterizes thermosets, and the processing requirements for thermosetting resins and polymers.

The three representative thermosetting materials are fabricated using condensation polymerizations. A critical aspect of these reactions is the generation of either water or other potentially problematic by-products (e.g., hydrochloric acid). If these products are retained in the final waste form, they can cause severe reductions in important properties. For instance, consider water. It does not interact strongly with the largely hydrophobic matrix and, hence, collects as liquid within the matrix. As a minimum consequence, this entrapped water reduces the overall loading of waste. More typically, the entrapped water can migrate throughout the matrix (e.g., via an evaporation-condensation mechanism) and thereby redistributes itself. A possible manifestation of this phenomenon is the problematic standing water that accompanies the solidification/stabilization efforts using urea-formaldehyde (UF) resins [385]. However, it is noteworthy that the miscibility with water that the emulsified UF-reagents exhibits makes the UF-based matrices somewhat attractive for the disposal of radioactive wastes [496].

Advantages of the UF-based matrices and related condensation polymers generally reflect their potential to encapsulate a variety of wastes. Examples include organic chlorides, phenols, paint sludges, cyanides, nickel-cadmium battery wastes, and dewatered and dried chlorine product wastes [503].

Another advantage is that some thermosetting resins can have a greater capacity for waste (i.e., approximately 30 wt %) than cement-based matrices and that they can incorporate dewatered waste that has not been dried. Recent results obtained with thermosets prepared from unsaturated polyesters demonstrate the ability to encapsulate a high level of borate waste, viz., in the vicinity of 50 wt % [506]; water-extensible polyester resins have similarly high loadings [500]. Radioactive wastes have been successfully encapsulated in thermosets based on unsaturated vinyl ester [498], using a commercial process that has been approved by the Nuclear Regulatory Commission [385]. Related processes involve the use of vinyl ester styrene (VES), which has been developed for hazardous, radioactive, and mixed wastes [497,501,505,511,515,517]; these are primarily suited for encapsulation and can be adapted to either batch or continuous processing schemes [516]. Tritium wastes have been successfully incorporated into an epoxy resin [507]. Polyester waste forms have been also used to incorporate spent and radionuclide-containing ion-exchange resins [508,509].

Lastly, other advantages are that thermosets typically have low densities (viz., approximately 1300 kg m^{-3}) and the solidified resins are generally not flammable [509]. The low densities ensure that waste forms composed of these materials are easy to handle and to transport.

An important disadvantage of thermosetting resins is a manifestation of one of its advantages. Specifically, the ability to encapsulate a variety of wastes reflects the inability to chemically react with many hazardous waste species. Consequently, chemical stabilization is typically not achieved [276,385,503]. Furthermore, the thermosetting encapsulation process does not render soluble hazardous species insoluble, and it does not detoxify or destroy hazardous constituents [101].

The strongly acidic catalysts that are required for the fabrication of UF-based waste forms, for instance, may enhance the solubilization of waste species, and some of them can attack the equipment and containers used, making the selection of materials for these processing parameters an important concern. Both the water used in the starting components, for example in emulsified reagents, and that generated via the central condensation polymerizations, must be allowed to evaporate prior to full curing of the polymer. The necessary formation of water in many instances demands the use of secondary containment. Lastly, some thermosetting resins are biodegradable; UF-based resins are especially vulnerable to biodegradation.

Important disadvantages of VES include its permeability to gases and its lack of chemical stabilization for inorganic hazardous species [517]. The problematic transport of gases may be from within the waste form. These may be generated during the processing stage; entrapped air is a common example. Gases can also be released by the waste upon aging; for example, excess water can be released and migrate through the matrix to more reactive sites, such as the locations at which dehydrated salts reside, leading to osmotic problems of pressure gradients. Of course, gas permeability also can lead to the uptake of water from the environment of the waste form. These features make VES attractive for the encapsulation of debris and relatively unattractive for wastes that can easily react chemically and those for which the integrity of the local microstructure would be sensitive to the degree of hydration.

Thermoplastic Polymers. Thermoplastics from two major families, namely, bitumen and vinyl-based polymers were described, respectively, in Sects. 3.2.4 and 3.2.5. The discussions in those sections and the information in Tables VII and X clearly reveal that these materials have markedly different microstructures. The microstructural differences are primarily qualitative, and they are critical to the control of these materials and their processing.

Whereas bitumen is a colloidal dispersion and not a solid in the typical sense, the vinyl-based polymers are true solids, which may be partly or extensively crystalline and whose properties stem from the behavior of the coiled macromolecules of which these materials are comprised. Moreover, it has been demonstrated in the earlier sections that both bitumen and vinyl-based polymers can be reacted with cross-linking agents, and the resultant cross-linking increases the rigidity of these materials. Extensive cross-linking is not possible for bitumen, and, in vinyl-based polymers that retain thermoplasticity after cross-linking procedures, the degrees of cross-linking do not approach that for typical thermosets. Lastly, the earlier discussions also stressed the behavior of these thermoplastic materials during processing, especially the properties of the vinyl-based polymeric melt, which exhibits a glass-transition region upon cooling and the advantages of casting prior to the curing stages.

Both families of thermoplastic materials exhibit some common advantages and disadvantages. Each type of matrix generally adheres well to insoluble waste components, and the materials embedded in the matrix can be reclaimed, if desired [276]. These factors justify the use of bitumen [371,376,377,378,495] and thermoplastics such as polyethylene [495,510,512,513,514] and polybutadiene [101,499] as encapsulating media for a wide variety of wastes.

Other advantages also relate to the encapsulation mechanism in thermoplastic matrices. One is that the leaching rates are significantly lower than those for cement-based systems, especially for hydrophilic waste constituents and those that are readily soluble in aqueous media. Another is that these materials are generally resistant to attack by aqueous media and microbial degradation; although anaerobic attack occurs in bitumen, it is a very slow process [102].

Bitumen and vinyl-based polymers also exhibit undesirable properties that constitute disadvantages for the use of these matrices as final waste forms. The risk of fire exists with each type of matrix, possibly being greater when the waste contains strong oxidizing agents. Polyethylene is an example of one vinyl-based matrix with a low flash point. The flash point of this polymer is 250°C. Although this property has an associated risk of fire for polyethylene waste forms, much is known about its flammability, and methods to retard flammability in this and similar polymers are generally known [199].

Bitumen and vinyl-based thermoplastics also demand that the waste be dry, and the drying step can be energy intensive. Undried waste increases the rate at which waste species migrate out of the final waste form, owing to the basic incompatibility of the hydrophobic matrix and the aqueous solution.

Finally, regarding the generally shared disadvantages, the inherent plasticity of the waste-matrix mixture may demand special considerations for transportation for both bitumen-based and vinyl-based polymer final waste forms: that is, the conditions under which these thermoplastic final waste forms are transported may differ from those under which they are ultimately buried for disposal. The sensitivity of an individual waste form can, of course, differ from that of other thermoplastic waste forms, although their chemistry may appear to be similar. Softening and glass-transition behavior would be needed in order to specify the thermal sensitivities of bitumen and vinyl-based polymers, respectively.

The encapsulation of strongly oxidizing species, such as nitrate salts, into these organic matrices may lead to final waste forms that are capable of self-ignition. The broad variety of waste compositions that needs to be treated exacerbates this problem because the self-ignition capability is not likely to be easily predicted. Hence, reliable safeguards may be difficult to establish.

Some specific disadvantages of bitumen are noteworthy, in view of the fact that its microstructure differs from those of the other organic candidates. An unrealistic assumption that it is a universal matrix material has led to its selection, particularly in Belgium, France, Germany, Sweden, Switzerland, and the former Union of Soviet Socialist Republics, as a matrix for the incorporation of radioactive wastes [378]. It is particularly susceptible to swelling that is induced by the encapsulation of hygroscopic salts [385]. These salts attract water; dissolve in it, according to their solubility characteristics; and establish a high osmotic pressure gradient within the bitumen matrix. As pointed out in Sect. 6.1.2, the magnitude of this pressure may exceed 30 MPa [377].

Bitumen suffers an additional disadvantage regarding the encapsulation of iron-containing and aluminum-containing salts. These components can induce premature hardening, and processing equipment can become clogged and damaged by abrasion [366,372]. Another disadvantage is that the high flash point, typically in the range of 250 to 300°C, can be lowered to unacceptable values by the incorporation of wastes [378].

Lastly, microbial attack of bitumen is possible under conditions replicating those in a repository [373,374, 375,378]. This degradation occurs either aerobically or anaerobically [374], though the degradation is minor when ideal aerobic conditions prevail [373,375]. However, in addition to a degraded matrix, aerobic and anaerobic attack can lead to the production of carbon dioxide. In turn, this gas may reduce the pH to the extent that encapsulated metals corrode and hydrogen gas, an explosive material, is generated in the process [374].

Summarizing Comments. The discussions in Sect. 3.2, the information in Tables VII, IX, and X, and the review of waste-containing organic matrices just given lead to the conclusion that neither the thermosetting nor the thermoplastic waste forms are sufficiently developed to be considered as baseline technologies today. Much development is needed within each generic group. The predominance of encapsulation as the immobilizing mechanism and the virtual lack of chemical stabilization underpin the general utility of the organic candidates. Unfortunately, the driving forces that operate on the encapsulated oxides and other salts of metals are very great and act to segregate the forms of waste components from the hydrophobic matrix. In general, the encapsulation of waste is not accompanied by chemical stabilization. Hence, upon destruction of the matrix such as is accomplished in leach tests (e.g., toxicity characteristic leach procedures, or TCLP), waste can be easily released, despite the inherent high resistance of the matrix to leaching.

Nonetheless, the pragmatic ability to encapsulate a wide variety of hazardous, radioactive, and mixed wastes in thermosetting and thermoplastic systems is not trivial. The kinetic factors are more favorable for encapsulation in thermosetting matrices. If the kinetic factors in thermoplastic systems establish overwhelming barriers to the migration of waste species, then these waste forms can be used. Recently, this type of encapsulation was successfully demonstrated for mixed waste ash, using polyethylene [518].

Generally, the thermoplastic waste forms can be tailored to outperform thermosetting waste forms, which suffer from the general disadvantage that the waste-matrix system cannot be reworked if the initial distribution and state of waste components are not optimized.

Bitumen is fundamentally not a polymeric system in the same sense that vinyl-based polymers are. Hence, the continuous fluid phase in bitumen waste forms, which has very low relative values for viscosity and density (i.e., compared with the corresponding values for the continuous phase in

vinyl-based polymeric waste forms), will flow. Consequently, secondary containment is mandatory for the successful use of bitumen for waste disposal. Constrastingly, the technical limitations that this microstructurally derived property sets are counterbalanced by the ease of formulation, adherence of the matrix to the encapsulated waste, and general availability of the raw materials or starting components used to generate bitumen waste forms.

With regard to the general ease of encapsulation that thermoplastic matrices provide, it is notable that they do not initially contain water that can promote oxidation of metallic debris. As a result, the hazardous constituents in the debris waste are likely to remain immobilized much longer in these waste forms than in those based on water (e.g., cement-based grout and gypsum-based materials). Furthermore, thermoplastic materials are resilient and can absorb the energy that is required in order to expand without cracking. Although additives can produce limited chemical cross-linking, enhancing the strength and reducing the tendency for expansion, thermoplastic waste forms for debris must be designed to accommodate the tendency to expand when necessary [336].

6.2.3. Vitrified Matrices

Two types of vitrified glasses were described in Sect. 3.3. These are silica-based and phosphate-based glasses. The discussions in that section and the information in Tables VII and XI lead to the emphasis placed on silica-based glasses in the present section [474].

Silica-Based Glasses. The principal glass matrices are based on silica (SiO_2) and are classified according to the type of anion present [118,124]. The glasses that contain anions of the Group 16 (VI A) elements of the periodic table (e.g., oxygen, sulfur, selenium, and tellurium) are chalcogenide glasses.²⁰ Oxide

²⁰The glasses that contain anions of the Group 17 (VII A) elements (i.e., fluorine, chlorine, bromine, and iodine) are halide glasses. Fluoride glasses are the most common halide glasses, but these are not discussed in this section. As was pointed out in Sect. 3.3, beryllium fluoride (BeF_2) is the principal glass former for these materials [107], and the fluorides of many metals that often reside in hazardous and mixed wastes (e.g., zirconium, thorium, uranium, scandium, yttrium, chromium, aluminum, gallium, indium, zinc, cadmium, and lead [124]) are conditional glass formers. Notwithstanding the toxicity of the BeF_2 precursor, these glasses may be attractive for the S/S of selected wastes, and recent research demonstrates that fluoride species can be used to suppress the formation of crystals that do not contain fluoride [474].

glasses belong to this category, and SiO_2 is considered the primary glass former in these systems because it is capable of forming glasses without the addition of other chemical agents [111,124].

The metal species of other components, such as the oxides of iron, aluminum, and lead that might exist in hazardous and mixed waste or form during the melting stages in the vitrification procedure, can contribute to the glass network; these metals are considered conditional glass formers if they contribute over 50 atom % of the cations to the network. Hence, the potential of hazardous metals to be chemically immobilized in the glass matrix relies, in part, on whether or not they are capable of acting thusly.

Vitrification, based on SiO_2 , has been examined in great detail for the S/S of radioactive waste, especially high-level waste [254,436,439,442,443,452,456,466,468]. Most of the successful applications have been achieved with borosilicate glasses (i.e., SiO_2 glasses that contain approximately 80 wt % SiO_2 and 13 to 15 wt % boron oxide, B_2O_3 [180]). The individual and collective efforts have led, in some cases, to the development of pilot- or full-scale operations [441,445,448,455, 456,459,466,468].

Some research has focused on the role of the basic glass composition, such as the effects of the glass formers used [440], whereas other studies have attempted to elucidate the matrix-related and waste-derived factors that affect the durability of the glass matrix [439,449,450,452,455,461,463,469]. Still, other investigations have focused on the formation of crystalline phases in the glass, either by devitrification [438] or sintering during hot-pressing procedures [453], and on some of the processing conditions that affect the off-gas composition [476]. Of course, the resistance of the glass toward attack by water and aqueous media and the leaching characteristics constituted major focal points of the studies on durability [436,455,456,461,466,468,481]. These investigations and others [98,100] reveal that the glass composition affects the chemical durability of the final waste form. However, they also demonstrated, collectively, that specific trends are not easily resolved. Often, this inability to identify specific trends stems from the variety of processing conditions used [98].

In addition to the temperature and composition, two of the major factors stressed in Sect. 3.3, the type of vitrification process is also an important variable when attempting to identify the underlying causes for discrepancies in the data obtained from vitrified final waste forms. The state-of-the-art method for radioactive wastes is based on a liquid-fed ceramic melter [457]. This technology converts a mixture of high-level liquid waste and glass-forming frit to a borosilicate glass and does not require

precalcination steps. Alternative technologies include a joule-heated ceramic melter, spray-calcliner/calcine-fed ceramic melter, and in situ vitrification,²¹ among others [254,457].

A discussion of these techniques is beyond the scope of this report. However, each produces glasses of similar overall composition. The degree to which the composition in the final specimens is microstructurally uniform and the sensitivity of the spatial distribution of species to the specific composition and the processing conditions are largely unknown. However, this situation is likely to improve as current analytical techniques are applied to these problems, as has been done recently in measuring the magnetic susceptibility of the glass as a function of temperature in order to obtain an indicator of the ferrous-to-ferric ion ratio in the glass.

Nevertheless, the general inability to relate the properties obtained with one type of process and a variety of wastes to those observed with other processes and wastes apparently derives from the lack of uniformity with which the different studies were conducted. This nonuniformity in processing and composition, which characterizes the broad range of studies conducted to date, apparently reflects the fact that the predominant objective of these studies has evolved into attempts to pass performance requirements. Consequently, the fundamental information that is required in order to predict performance in a general fashion is often lacking. When this type of information is available, it is often restricted to a single vitrification process and a narrow range of wastes that do not represent the many types of wastes of concern under FFCA [277].

Contrasting the abundance of research that has been conducted on glass waste forms for high-level waste, relatively little attention has been paid to the use of glass waste forms for hazardous and mixed waste [278]. However, some have begun to emerge in the open technical literature [471,475]. A general lack of information on the application of vitrification techniques to the treatment and disposal of hazardous and mixed wastes exists. This situation leads to the conclusions that silica-based and borosilicate glasses have the potential for adequately encapsulating many RCRA metals and that some of these may be

²¹In situ vitrification is a method by which selected hazardous waste, typified by contaminated soil, is immobilized without removing it from the storage or disposal area [385]. In the application of this technique for soil, an electric current is generated between two electrodes that have been embedded in the soil. This current melts the waste at a temperature that approaches 2000°C. Upon cooling, the melt solidifies and produces a glass-like material that immobilizes the waste residue. This approach has received attention in recent years, particularly for high-level wastes [444,458,460,464,465,467,477].

chemically immobilized if they behave as conditional glass formers; see Sect. 3.3. Much more research is needed in this area. Still, the achievements realized for high-level wastes support the attempts to apply vitrification to the S/S problems of hazardous and mixed wastes.

The compositional range for hazardous and mixed wastes both greatly differs from and is more varied than that of high-level wastes. Hence, different glass formulations are likely to be needed in order to achieve chemical stabilization of the wastes and their residues after vitrification. The chemical requirements for cationic metal waste species to contribute to the glass matrix (i.e., in a fashion akin to that of conditional glass formers) provide guidance for the chemical stabilization of wastes that contain ionic metal species. Those wastes that do not meet these requirements must be encapsulated, based on the currently available information. Metal-containing compounds that act as glass modifiers, compounds in which the metal is retained in anionic species (e.g., $\text{Cr}_2\text{O}_7^{2-}$), and residues from organic waste probably belong to this group.

Silica-based glasses, including borosilicates, exhibit important properties that constitute advantages as waste forms for radioactive wastes, and these have been exploited most for high-level wastes. They are generally chemically durable waste forms, also resisting biological attack. A wide range of compositions, based on many combinations of conditional glass formers and silica, the primary glass former, provides a degree of flexibility for S/S that is often superior to other waste forms. Common additives are abundant and can be obtained readily. The silica-based waste-form glasses do not typically contain free liquids because the high temperatures required to prepare the melt converts compounds that are free liquids at ambient temperature to solid and gaseous products; oxidation and decomposition are the pathways most often occurring in this conversion. The capability of the solidified melt to encapsulate waste ensures a high waste loading in many instances, although the chemical stabilization limit may be relatively low. Lastly, secondary containment is not usually required.

Silica-based glasses do possess some disadvantageous properties. The solubilities of many wastes are low in the glass melt. This feature corresponds to the inability of many species that are not conditional glass formers to form covalent bonds with the siloxane (i.e., $-\text{Si}-\text{O}-\text{Si}-$). Also, the vitrification process can generate gases that limit the rate at which waste is incorporated into the glassy matrix [278]. Oxides of sulfur, nitrogen, and carbon are among these problematic off-gases. The generation of gaseous water,

hydrogen, and halogens would be troublesome. The presence of these gases demands scrubbers and related equipment in order to treat them adequately.

The solid-state solubility of waste species can be low in the cooled glass. This situation can lead to precipitation upon cooling or to uncontrolled recrystallization. The latter may not be evident for long periods of time, even years. Either process can ensure that the hazardous species become more available to the environment in which the waste form is stored: that is, the surrounding glassy matrix can be mechanically degraded, via internal or externally generated fracture, or chemically degraded, as would be the case with corrosion of the glass by the environment. Upon such degradation of the glass, the encapsulated compounds formed by either nucleation event become exposed to the environment.

The most overriding shortcoming of vitrification processes to S/S of hazardous and mixed wastes is that only limited data on the applicability of SiO_2 -based glass to such wastes have been gathered. The high temperatures developed during vitrification are in the vicinity of 1350°C , and, consequently, some waste constituents may vaporize during processing (e.g., Cs species).

Phosphate-Based Glasses. These glasses are based on phosphorus pentoxide (P_2O_5), which is a primary glass former; see Sect. 3.3. These glasses can be formulated with alumina (Al_2O_3) in order to establish a microstructural network akin to that in silicate glasses. Other conditional glass formers, such as lead oxide (PbO) and other polyvalent metal oxides, can also be present. Their roles can be anticipated to resemble that of Al_2O_3 .

Phosphate glasses can be tailored for specific applications, and many of these glasses are based on sodium phosphate glass. Extensive research on waste forms for nuclear waste reveals that lead-iron (Pb-Fe)²² phosphate glasses exhibit useful properties for the S/S of high-level radioactive waste [454]; lead-aluminum phosphate glasses have also been examined for these purposes [437].

Most waste oxides were found [454] to dissolve in the Pb-Fe phosphate glass melt completely (i.e., when suitably prepared and at 1050°C). These glasses resist corrosion by natural groundwater, at ambient

²²These metals are present as oxides.

temperature when the pH resides in the range set by pH 5 and pH 9. Above 150°C, the formation of phosphoric acid drives the hydrothermal corrosion of these glasses.

These glasses were, however, susceptible to an increased corrosion rate in the presence of a concentrated saline solution (viz., sodium chloride, NaCl) [454]. However, at an elevated temperature of 90°C, the corrosion rate induced by brine was found to be sensitive to the PbO-to-Fe₂O₃ ratio; the corrosion rate decreased with increases in the Fe₂O₃ content and concurrent decreases in the PbO content. Importantly, although devitrification was not observed after raising the temperature to 500°C and annealing the glasses for extended duration (450 h), crystallization was found to occur during the cooling of the melt if the cooling rate was less than the range 1 to 10°C per minute [454]. The maximum rate of crystallization occurred when the temperature was in the vicinity of 680°C.

Apparently, phosphate-based glasses have not been studied regarding their potential as final waste forms for hazardous and mixed wastes. The research conducted on the use of lead-iron phosphate glasses for S/S of nuclear wastes [454] and recent efforts to characterize the microstructure of sodium phosphate glasses [130], amorphous newberyite (MgHPO₄·3H₂O) [130], and lead phosphate glasses [130,131] indicate that this type of glass may hold great potential for selected wastes. Specifically, the incorporation of aqueous sludges appears promising, if the composition and microstructure can be tailored. The cited research implies that they can be controlled in order to exploit this matrix for waste disposal purposes.

Summarizing Comments. Vitrified waste forms, especially silica-based glasses, have proven successful in many waste solidification/stabilization (S/S) applications. Numerous investigations focus on high-level radioactive waste [436,439,442,443,452,466,468] and the development of pilot- or full-scale operations [441,445,448, 455,459,466,468]. These successes are realized by attending to the interrelationships that comprise the paradigm described earlier (Sect. 5). Much of the research cited in Sect. 3.3 and in the present section relied on careful analyses of the compositional and microstructural features of the waste-free and waste-containing matrices. When these were used to interpret the various types of processing behavior and the ultimate properties of the solid system, the range of uses for silica and borosilicate glasses was greatly expanded.

These applications underpin the potential for silica-based glass for uses in the S/S of hazardous and mixed wastes. As already stated, the most significant limitation is the dearth of investigations on these wastes. This general lack of information and the related limited understanding of the compositional and processing effects on the development of the microstructure are most pronounced for wastes that do not contain metal compounds, on the one hand, and phosphate-based matrices, on the other.

In view of the fact that vitrification is a baseline technology for the DDT&E Program, it is noteworthy at this point that this matrix is inadequate for all wastes [278]. Some important waste species can leach too readily from silica-based glass if corrosion and dissolution of the matrix predominate. Lastly, off-gases and volatile waste species can be troublesome, and the resolution of the problems that they engender can complicate the design of a vitrification process.

6.2.4. Devitrified Matrices

Devitrified glasses were described in Sect. 3.4, and these matrices are referred to as glass-ceramics. The discussions in that section and the information in Tables VII and XII indicate that the two main classifications of glass-ceramics that demonstrate a range of properties that are generally sought in final waste forms for hazardous, radioactive, and mixed wastes are based on alkali and alkaline earth silicates and aluminosilicates. Other families exist, and they were summarized earlier.

Glass-Ceramics. These matrices are produced by the controlled crystallization of glasses with the appropriate compositions; see Sect. 3.4. Fine crystals reside in a residual glass. The composition of each phase depends on the initial composition of the melt; the processing variables used to make the precursor glass, especially the temperature to which the initial reagents or starting materials are raised and the rate of cooling; and the thermal treatments that constitute, in part, the annealing procedures. These aspects combine to generate the glass-ceramic assemblage. The nature of the crystalline microstructure sets the properties of the matrix, and the tailoring of it can be used to optimize the S/S of hazardous, radioactive, and mixed wastes using glass-ceramic matrices.

Glass-ceramics have been examined for the disposal of radioactive wastes [97,98,100,254, 278,484,485]. A major advantage of glass-ceramics that are based on silicates is that the deliberate conversion of a glassy matrix to a glass-ceramic eliminates the problems which ensue from the accidental devitrification

of glasses upon cooling and during storage and burial [484]. Another benefit that derives from the use of glass-ceramics, as compared to the use of glass, is the greater mechanical stability and the increased resistance to cracking and to fracture imparted to the matrix by the crystalline phases. Additionally, glass-ceramics typically exhibit high durability regarding the susceptibility to chemical attack. The solid phases are typically more thermodynamically stable under the use conditions than the glassy analogs are.

In view of the range of chemical compositions that are possible in glass-ceramics, as suggested by Sect. 3.4, the potential types of matrices that this range implies can be deemed [484] to be superior to many other waste forms, especially regarding waste ions. A major obstacle to their development is that the composition of the primary crystalline phases must be tailored to the needs of the waste composition and physical state. Regarding the thermodynamic stability of the waste-form matrix, only the residual glassy phase would generally be far from equilibrium; the solid ceramic phases are, as just stressed, closer to equilibrium. Considered in toto, the glass-ceramic system is closer to equilibrium and, therefore, is more likely to be less reactive and more chemically durable than the corresponding glass having the same overall elemental composition.

Notwithstanding these advantages, some disadvantages exist. The chemical aspects are typically complex, and the relationships among the chemical aspects, processing variables that provide for an optimized glass-ceramic microstructure, and desired properties can be quite complicated. It may be necessary to assess the varied time-temperature-transformation behavior of glass and glass-ceramic systems [137] and the effects of waste species on them [478,480,482]. Of course, the presence of water can alter the conclusion just described regarding the thermodynamic stability and resistance to chemical attack: that is, some crystalline phases may exhibit relatively high solubility in aqueous media.

An example of this phenomenon is provided by the glasses comprised of soda (i.e., sodium oxide, Na_2O), baria (BaO), and silica (SiO_2). A composition in the melt of 67 wt % Na_2O , 17–23 wt % BaO , and 16–10 wt % SiO_2 can be processed to yield a glass that is x-ray amorphous [110]. Upon annealing at temperatures that approach 1000°C , crystallization of BaSi_2O_5 can be induced, either with or without the aid of metal particles (Sect. 3.4), providing crystals having a variety of morphologies that can be controlled. The sodium-rich, sodium-silicate-like glassy matrix is highly soluble in aqueous media and upon dissolution leaves a suspension of finely divided BaSi_2O_5 [484]. In this case, the glassy matrix is very soluble. Based on the physicochemical similarities between the BaO -containing glasses just

described and soda-lime glasses (lime is calcium oxide, CaO), adjustment of the compositions in the crystalline and glassy phases of the Na_2O - BaO - SiO_2 system, for instance by the presence of boria (B_2O_3), is anticipated to significantly reduce the aqueous solubility of the glassy phase: that is, the overall system is closer to equilibrium both in the absence of water and in its presence. An even more stable system regarding dissolution of the phases in the presence of aqueous media is achieved by substituting alumina (Al_2O_3) for the B_2O_3 [484]. This type of glass-ceramic belongs to the family of aluminosilicate glass-ceramics.

Another restriction stems from the effects of radiolytic processes on the glassy and crystalline phases in glass-ceramics. Accelerated corrosion, enhanced leaching, and related radiation-derived phenomena have been documented [446,447,472], and the swelling that occurs upon exposure of the materials to radiation can lead to an increased corrosion rate [472] and degraded mechanical properties [181]. Similar problems can be anticipated for glass-ceramics. However, the effects of radiation-induced swelling would appear to be more pronounced for the crystalline phases than for the glassy regions [435,451,479].

Still, the potential exists for the crystalline phases in glass-ceramics to become amorphized by radiation capable of inducing ionization or displacement effects. Although some of the crystalline phases may have mineral analogues that have survived self-radiation over geologic duration [411], many of the phases that can be produced in glass-ceramics [137] have no natural analogues. Hence, no basis currently exists for the prediction of the long-term stability of these phases. Some existing techniques can be applied in order to investigate the amorphization process. Examples include in situ transmission electron microscopy and He ion irradiation [424,483]. Such research has indicated that different ceramic phases possess different abilities to recover their crystallinity after exposure to such radiation. Further, specimens with damage caused by area-based radiation doses in the range 10^{15} – 10^{17} He^+ cm^{-2} can demand subsequent annealing at temperatures up to 1000°C in order to regain their crystallinity [424].

Lastly, there are virtually no data available on the systematic examination of glass-ceramic materials as final waste forms for hazardous and mixed wastes. The appearance of some recent reports indicates that this situation may change [483,484,485,486], but high-level wastes tend to be emphasized. Hence, the current scale of glass-ceramics as final waste forms is taken to be laboratory scale, especially with regard to their use with hazardous, low-level radioactive, and mixed wastes.

Summarizing Comments. The chemical aspects of microstructural development and the microstructure itself are complicated. However, suitable materials have been developed for high-level radioactive wastes, and the properties of these matrices can be superior to those of alternative waste forms. Notable technical features of this class of materials are offered in the discussions in Sect. 3.4 and the information in Tables VII and XII.

As for the S/S of high-level waste, the successful incorporation of hazardous waste species depends on the interrelationships among the chemistry, the processing scheme, and the development of the microstructure. The control of the chemistry used to obtain the precursor glass and the assessment of microstructural features developed in the glass and upon devitrification during annealing are mandatory for the successful identification of useful processing cycles and the concomitant limitations on the matrices produced.

6.2.5. Ceramic Matrices

Ceramics were briefly described in Sect. 3.5. The discussions in that section and the information in Tables VII and XIII indicate that many specific ceramics exhibit useful properties for the S/S of hazardous, radioactive, and mixed wastes. Many are unary metal oxides, whereas other important oxygen-based candidates are silicates, aluminates, phosphates, and titanates.

Oxides and Oxygen-Based Ceramic Matrices. These materials may be considered to be either single-component or multicomponent ceramics. Although these designations are arbitrary, they help to distinguish the oxides in which only one metal is considered to be in the cationic state from the more complicated materials in which two or more metal species exist. Alumina (Al_2O_3), rutile (t-TiO_2), zirconia (ZrO_2), and hematite (Fe_2O_3) typify the family of single-component oxides. Mullite, spinels, and Synroc are examples of the second group. Mullite is a crystalline aluminum silicate with the formula $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Spinel is a crystalline refractory oxide with the general formula AB_2O_4 , in which A is a divalent metal or mixture of divalent metals and B is a trivalent metal; MgAl_2O_4 , $(\text{Fe,Ni,Mn})\text{Al}_2\text{O}_4$, and NiFe_2O_4 typify the members of this family. Synroc is a mixture of ceramic phases. The principal ones that are relevant to waste-form applications are perovskite (CaTiO_3), zirconolite ($\text{CaZrTi}_2\text{O}_7$), and hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$) [100,410], although spinels may also be present [406].

Ceramics have been extensively examined as potential waste forms for radioactive wastes [97,98,99, 100,171,254,272,278,407,408]. The majority of efforts that identify long-lasting results that can be tailored in a variety of circumstances focus on Synroc or its titanate-based component ceramic phases [401,402, 406,409,411,420,425,426]. Synroc exhibits properties that constitute significant advantages as a waste-form matrix for the S/S of radioactive waste, particularly high-level waste. These advantages derive from the intrinsic properties of the ceramic. The significantly higher resistance to leaching by groundwater, both under ambient conditions and at elevated temperatures (i.e., in the range from 95°C to 150°C), compared with that of borosilicate glass, is chief among the attractive properties [411,434]. The Ti- and Zr-rich oxide phases confer this superior stability in the presence of aqueous media. Many of the intrinsic leachabilities for high-level waste species are on the order of 0.1% of those for borosilicate glass, which is a commercial waste form for the immobilization of high-level wastes generated in the reprocessing of nuclear fuel [411].

These results reflect the fact that, in many instances, the radioactive species can be chemically immobilized in the Synroc microstructure. This stabilization is achieved by adjusting the processing conditions to those that ensure the formation of dilute solid solutions of the radionuclides: that is, the species of concern are incorporated into the crystal structures of the ceramic phases that form in Synroc. They can also dissolve at high temperature into any glassy, intergranular phases that survive the sintering process [410].

The existence of a passivating layer of rutile and its effect on the leach rate have been proffered as part of the explanation for the reduced leach rates that are characteristic of Synroc [401,402,405, 411,433,434]. The surface layers of Synroc become increasingly rich in TiO_2 as the monovalent and divalent cations leach out. This TiO_2 -rich layer may act as a protective layer and impede the further leaching of waste and matrix constituents from the interior of the grains.

This microstructural contribution to the improved waste-form properties of Synroc partly underscores the studies of rutile ($t\text{-TiO}_2$) as a waste form for radioactive waste [414]. Indeed, rutile possesses some attractive properties, including superior leaching properties, when compared with borosilicate glass. Unlike Synroc, the single oxide can effectively encapsulate waste, while maintaining very low leach rates for the radioactive constituents [414]. This finding suggests that, whereas the intimate mixing between the matrix precursor powders and the solid waste is desirable, acceptable microstructures and properties

can still be obtained when the optimum degree of mixedness is not achieved. Lastly, the loss of radionuclides during processing, owing to their evaporation, may be much less for TiO_2 than it is for borosilicate glass [414].

Some research has examined phosphate-based ceramics for similar purposes. In particular, monazite, which is a mixed lanthanide orthophosphate (LnPO_4 , where $\text{Ln} = \text{La}, \text{Ce}, \text{Nd}$), exhibits attractive properties for radioactive waste [413]. One of the important findings is that waste loading that can be realized with monazite ceramics is on the order of 10 to 20 wt % simulated high-level waste. Although this level is similar to that for borosilicate glass, equivalent mass ratios favor the ceramic host: that is, the densities of these phosphate-based ceramics are normally between 4000 and 5000 kg m^{-3} [413], whereas an approximate value for the density of borosilicate glass is 2200 kg m^{-3} [180]. Based on equivalent mass concentrations of waste in each type of matrix, approximately twice the radionuclide mass is incorporated per unit volume in the ceramic waste form as is incorporated in the glass waste form. Hence, for a given mass of waste, the monazite solidifies it into a less voluminous product. Analogous to the leach results just described for Synroc, those for monazite waste forms also exhibit marked improvement when they are compared with the leaching behavior of borosilicate glass [413]. The very low solubility of the rare-earth phosphate matrix in aqueous media is a major contributing factor to this performance.

Other ceramics that have been investigated as potential waste forms for radioactive wastes include spinels [412,415]; clay-based ceramics [404,418]; other phosphates, such as sodium zirconium phosphate [408,415] and magnesium-based and zirconium-based phosphates [419,427,428,432]; alumina [98]; and spent nuclear fuel [416,417]. The principles that have been previously emphasized in this section have also been observed to operate for these candidates too.

Both the advantages and the disadvantages of ceramic matrices parallel those of glass-ceramics; see Sect. 6.2.4. Differences exist between these two families of matrices. The main ones relate to the processing routes (viz., the formation of a precursor glass for glass-ceramics and the annealing stages that follow it for glass-ceramics and the powder processing-sintering routes to the ceramic materials addressed in the present section), to the effects of the relative degrees of crystallinity in each case, and to the generally higher resistance of ceramics toward amorphization upon irradiation that induces ionization or displacement effects.

In view of the fact that each ceramic family has a very wide compositional range within which to work, solubility issues, leaching characteristics, microstructural phases, and processing aspects vary widely for candidate ceramic waste forms. However, their inclusion in serious attempts to understand the mechanisms by which improved waste forms can be prepared highlights the wide compositional range that is available. In this regard, many of the advantages described in the previous section for glass-ceramics are shared by many of the potential ceramic waste forms. In the case of crystalline ceramics that are prepared using powder processing and for which melt processing is not used, the potential for chemical stabilization hinges on the ability to incorporate waste species into the chemical network (i.e., the atomic arrangement within the crystalline grains): that is, the waste species must be in solid solution.

When this state is not fully achieved, the encapsulation of waste remains viable and feasible. The nearly theoretically dense ceramic matrix grains and the encased grains of waste residue, which are likely to be ceramic themselves, severely limit the ability of environmental components to reach the interior of the matrix-waste composite system. Accordingly, the migration of waste species from the encapsulated grains is extremely retarded in these systems.

Sufficiently broad ranges of compositions, processing methods, and microstructures are available with this class of waste-form matrix. Properties, such as low solubility and high resistances to externally generated chemical and mechanical forces, can be anticipated.

Ceramic Descendants of Waste. The inherent stability of ceramics underpins the general goals in some treatment schemes. Furthermore, these treatments can represent a great variety of wastes.

Consider the combustion processes that are designed to convert hazardous organic and mixed organic-inorganic waste to less hazardous forms. The ashes that are produced during the combustion of hazardous wastes are generally ceramic materials. Few of these inorganic ashes exhibit hazardous characteristics that require further treatment, and those that retain hazardous characteristics generally do so because their component phases have high aqueous solubility or chemical reactivity under ambient conditions. Hence, these ashes demand further immobilization procedures prior to their disposal. Without this step, they can easily liberate hazardous metals over long periods of time. This release occurs when either the ashes contain high concentrations of metastable hazardous phases or they are

embedded in a glassy phase of inherently nonhazardous material (e.g., silicates) that is relatively soluble or reactive with the environment. In most of the latter cases, the retention of high concentrations of alkali and alkaline earth minerals appears central to the undesirable properties of the ashes.

Nonetheless, the general inertness of the ashes (i.e., in the short term) is widely recognized. This behavior and the corresponding understanding are based on the ceramic structures in these materials. Similarly, the soils and solid by-products of thermal desorption processes [164], such as those used to remove hazardous organics from contaminated soils, possess ceramic or mineral-like phases.

A second treatment that demonstrates the recognition accorded the stability of ceramic forms of hazardous waste species is provided by the use of sulfide reagents in order to convert hazardous metal species to metal sulfides [152,280]. Many RCRA metals form metal sulfides, and the aqueous solubility of these is generally much lower than that of the corresponding metal oxides. As a consequence, the metal sulfide is the less likely of the two ceramic forms to be attacked by water and to liberate the hazardous metal. Iron(II), Co(II), and Ni (II) form relatively stable sulfides. Of course, even these sulfides must be stabilized further using S/S techniques because oxidizing conditions and acidic environments can markedly increase the solubility of the metal species [152,280]. Still, the fact that metastable ceramic sulfide phases are sought in some treatment schemes underscores their desirable features.

Still, a third treatment that demonstrates the general objective to convert wastes to ceramic forms is the conversion of nitrate-containing, hazardous and radioactive aqueous wastes to ammonia and ceramic by-products [421,422,423,429,430,431]. The conversion is accomplished by reacting the nitrate species with metallic aluminum under alkaline conditions in order to produce ammonia and to precipitate the metal species as aluminates that can be further transformed to hydrated oxides. This process is called the NAC process, emphasizing the conversion of nitrate to ammonia and ceramic, and has demonstrated that 85 to 99% of the nitrate present can be converted to gaseous ammonia while producing a ceramic by-product that has the potential to act as its own waste form [431]. The principal ceramic produced is hydrated aluminum oxide, typically as gibbsite, which is one of the main mineral phases in bauxite [60] and is the best known aluminum trihydroxide [53]. Other aluminum (hydrous) oxide polymorphs can be obtained by calcination, if desired [60]. When silica is present, it leads to aluminosilicate ceramic products [421].

The hazardous and radioactive metals in the original waste that also precipitate are retained in the insoluble aluminate phase first formed. The reaction that transforms the amorphous aluminum hydrous oxide to crystalline gibbsite can also convert the hazardous and radioactive species to less mobile ceramic forms.

Hence, the chemical stabilization of these species is promoted by the careful conversion of aqueous waste to ceramic descendants. This conversion of undesirable mobile waste species to less immobile ceramic counterparts is shared by the two preceding treatments and is founded in the recognition of the inherent thermodynamic stability of many ceramic phases.

Summarizing Comments. The chemical aspects of microstructural development and the microstructure itself are complicated aspects of ceramic matrices. Suitable materials have been developed for the disposal of high-level radioactive wastes, and the properties of these matrices can be superior to those of alternative waste forms, notably borosilicate glass. Some of the technical features that combine to permit this type of development were discussed in Sect. 3.5. The central features of ceramic matrices resemble those of glass-ceramics, as described in Sects. 3.4 and 6.2.4 and Tables VII and XII.

As has been stressed throughout this report, the successful incorporation of hazardous waste species into a solid matrix depends on the interrelationships among the chemistry, the processing scheme, and the development of the microstructure. This finding is particularly important for ceramic waste forms because their usefulness is predicated upon the development of crystalline grains and the assemblage of these grains.

The use of ceramic matrices for the S/S of hazardous, radioactive, and mixed wastes relies on the simultaneous manipulation of a wide variety of atomic and molecular species in such a manner that they establish precise arrangements. Perhaps, the success of ceramic waste forms is more sensitive to the attention with which this effort is undertaken than is the case for the previously described candidate waste forms. Hence, the control of the chemistry used to obtain the ceramic phases of both the matrix and the ultimate waste residues and the assessment of microstructural features developed in the final waste form are critical to the successful application of ceramic waste forms. Certainly, they represent the most thermodynamically stable encapsulations for many varieties of waste.

6.2.6. Metallic Matrices

Two types of metallic matrices can be envisioned for the solidification of hazardous, radioactive, and mixed wastes. Each has limited applicability for the present purposes.

One type of matrix is used for the encapsulation of either glass or crystalline ceramic phases in which waste species are solidified [415]. These composite systems are multibarrier matrices. In them, the metallic continuous phase acts as a secondary encapsulation medium. Such composite systems are complex. A few of the advantages and disadvantages that have been identified for the solidification of high-level radioactive waste using such matrices are given in Table VII. In view of the facts that the metallic phase establishes a condition of secondary encapsulation and that the chemical aspects, the processing requirements, and the development of microstructure are too varied to be adequately treated here [90,94,415], these matrices are beyond the intent of the present efforts.

The second type of metallic matrix is an alloy: that is, two or more metals are coprocessed in order to establish an intimate, atomic-scale mixture of the elements that permits the mutual interdiffusion of the constituent metal [174,175,176,179]. Solidification from the melt is typically the route by which these materials are prepared. The resultant alloy may be amorphous or crystalline.

Matrices of such metallic alloys can be used to encapsulate waste. However, they have not been actively pursued for this purpose. Their use is plagued by some inherent problems, such as the ease of oxidation and the tendency to corrode. These problems reflect the thermodynamic instability that characterizes the majority of metallic alloy matrices under the storage and burial conditions.

The chemical stabilization of waste in metallic matrices is essentially restricted to hazardous metals. Waste liquid mercury is such a candidate for this type of stabilization [363]. Some features of this S/S approach are given in Table VII.

The application of metallic alloy matrices constitutes a waste treatment rather than a waste-form technology. Indeed, amalgamation (viz., the preparation of alloys containing mercury) is the treatment standard for liquid mercury [364]. In view of the fact that this method of achieving chemical

stabilization is a treatment procedure, it lies beyond the assessment effort that this report addresses. Hence, metallic alloy matrices are not considered further herein.

7. WASTE-FORM PROPERTIES, REGULATIONS, AND PERFORMANCE CRITERIA

7.1. Waste-Form Properties

The descriptions and discussions in Sects. 3 and 6 lead to the central and critical conclusion that no single waste form, generically described in Tables VII, VIII, IX, X, XI, XII, and XIII, is suitable for each type of waste. Two important technical implications follow from this concept: namely, (1) the chemical and physical properties of each hazardous waste stream establish the technical requirements that must be met by acceptable candidate waste forms, and (2) the inherent properties of the composite, waste-matrix systems set, in turn, the relative technical priority for each candidate matrix.

These considerations lead to the selection of grout-based and glass-based matrices for the solidification/stabilization of many hazardous, radioactive, and mixed wastes: that is, grout and glass individually possess adequate and sometimes superior properties that justify their status as baseline technologies for waste disposal. However, as stated throughout this report, these waste forms exhibit properties that limit their use. The physicochemical aspects that underpin these limitations demand that alternative waste forms be developed. The potential benefits offered by other materials can include (1) an improved chemical durability (e.g., as manifested in a reduced tendency for leaching to occur), (2) an enhanced processing ability to tailor both the final composition and the microstructure in order to meet multiple criteria, and (3) the capacity for highly loaded waste forms.

An important inference, based on these considerations and their underlying technical aspects, is that many issues of cost reflect the technical complexities of individual waste-matrix combinations. These comprise, in part, the final-waste-form fabrication and the handling procedures of the final specimens. Alternatively, a costly waste form is one that represents a generally complex technology, an inefficient use of the available technology, or an underdeveloped technology. Whereas the costs of the raw materials or starting components and those regarding energy consumption are important, these can be viewed as secondary concerns when compared with the costs of storing and disposing of inefficiently solidified and stabilized waste.

7.2. Regulations

The applicable regulatory issues, which were briefly reviewed earlier (Sect. 2.3), demand that each type of hazardous waste and mixed waste described in Tables IV and V must be treated for disposal. Only those wastes for which no acceptable incineration, stabilization, and solidification technology exists may be stored. Consequently, the Resource Conservation and Recovery Act of 1976 (RCRA) [360,363,364] and the Comprehensive Environmental Response, Compensation and Liability Act (Superfund) of 1980 (CERCLA) [343,344,345,346] greatly influence the development of stabilization/solidification (S/S) technologies for such wastes [363]. These acts include, among other features, the provisions for the development of suitable criteria to identify hazardous waste, to set the standards for disposal facilities, and to encourage the establishment of state-based regulatory programs. Additional Congressional regulations address the generation, handling, treatment, and disposal of wastes, and CERCLA and its reauthorization in 1986 (SARA) established a massive remedial program for the cleanup of existing sites that constitute threats to the environment [147,343,344,345,346,365].

More recently, other risks have been considered in attempts to identify the hazards associated with waste materials, including the detrimental impact on the ecosystem [148,153,267, 268,269,321]. Clear-cut assessments are often not possible, owing to the generally incomplete state of knowledge that exists [154,155]. Land bans that result from the regulations just cited are designed to prevent the degradation of the environment when the residuals (e.g., smelter slag and incinerator ash) are treated for disposal in uncontrolled landfills or in the event that all the protective measures of secure landfills at treatment, storage, and disposal (TSD) facilities fail [363,364,365].

Summarily, these bans and the foregoing legislation impact the S/S technologies in terms of the land ban system and the delisting system [363,369]. The land ban regulations state, in addition to other provisions, that bulk hazardous waste liquids and sludges cannot be buried in landfills unless solidification of the liquid waste is successful through chemical means and not solely by physical absorption techniques. Legislation has also provided for the specification of the best demonstrated available technology (BDAT) [354,363] that is to be used in TSD facilities in order to reduce the concentrations of hazardous materials to levels below the maximum concentrations permitted. Many of these are subject to the toxicity characteristic leach procedures (TCLP) [360,362,363,364,370].

7.3. Other Waste-Related Issues

The constituents in the waste or those in the residuals from pretreatment that are specifically addressed by the various chemical fixation and solidification (CFS) technologies include volatile organics (e.g., acetone, benzene, carbon tetrachloride, and acrylonitrile); semivolatile organics (e.g., aniline, halogenated cresols, cyclohexanone, naphthalene, and nitrobenzene); metals (e.g., antimony, arsenic, barium, beryllium, chromium, lead, mercury, nickel, thallium, and zinc); nonmetal inorganics (e.g., cyanide, fluoride, and sulfide); and organochlorine pesticides [265,332,369]. Numerous sludges are also addressed by the aforementioned and related legislation [148,369]. The by-product sludges of electroplating, petroleum refining, heat-exchanger cleaning, steel finishing, ink washing, and pharmaceutical processing are a few of these targeted wastes; many of these are represented, either explicitly or implicitly, in Tables IV and V.

Analogous and often similar requirements apply to the disposal of low-level radioactive waste [172,259,262]. Importantly, the technical concerns regarding the disposal of low-level waste resemble those for the disposal of high-level waste, and many are identical [172,173]. This relationship often reflects the fact that many physical and chemical properties of low-level wastes resemble those of high-level wastes [168,171,173]. Hence, the advances developed for high-level waste forms can be adapted, in some cases, to the development of CFS waste forms for low-level radioactive wastes.

Nonetheless, the general lack of understanding regarding the incorporation of low-level wastes into many of the matrices described earlier (Sects. 3 and 6) and the large volume and diversity of low-level wastes demand that fundamental and applied research be conducted, respectively, in order to elucidate and adapt the basic sorption processes involved in the various stabilization mechanisms for these wastes. Clearly, this status and the need for appropriate research also apply to the immobilization of mixed wastes.

7.4. Performance Criteria

The resolution of the various issues raised in the previous discussion for individual candidate alternative waste forms requires a set of criteria by which the acceptable and superior properties of individual waste

forms can be distinguished from unacceptable ones. This set of criteria must be largely independent of the type of waste whose S/S is being assessed and suitable for meeting the applicable regulations and statutes. Furthermore, the criteria should include as many desirable technological, political, and social features as are reasonable. For instance, a waste-form technology that chemically stabilizes waste species is preferred to an otherwise equivalent one that simply encapsulates waste. Similarly, a waste-form technology that emits an offensive by-product, which is neither hazardous nor regulated, is politically and socially less desirable than other technically acceptable ones that do not generate such by-products.

Clearly, a complete list of criteria that encompass both the technically mandated requirements and the desirable features of a suitable waste-form technology would be impossible to compile. In addition to the awesome task of satisfying an innumerable array of concerns that such a list must address, the appropriateness of such a list would be transitory at best: that is, the specific requirements that must be met presently may not apply in the future, though the intent of the technical requirements may survive for a long time to come. For instance, it is insufficient to state that TCLP must be met. The intent of this statement will always apply in the foreseeable future. However, the values of the leaching index may change, probably to more restrictive values, as new information is gathered, as regulations change, as the political and social values evolve, and, possibly, as analytical tools improve. Hence, it is obvious that any list of criteria is arbitrary, including those that appear to address mandated issues.

Notwithstanding these inherent limitations, the properties that help to characterize an individual waste form and by which its performance can be assessed are compiled in Table XIV. Typical desired value or behavior is given for each property, along with a brief statement of the derivation underscoring the property or its assessment. The properties are listed in generally decreasing order of importance, and three subgroups are identified as high priority, medium priority, and low priority, in order to aid the interpretation of the compilation.

For the purposes of the FFCA and the DDT&E Program, the members that are assigned high priority are either regulated or critical to the implementation of the technology as an alternative baseline technology. The properties that are assigned medium and low priorities are desirable in many, if not most, instances. The last property, criticality, is included in the table, although its position is somewhat misleading. Within the broad scope of the various wastes described earlier (Sects. 4 and 6.1), fissile isotopes are

unlikely to be present in radioactive and mixed waste. Hence, criticality is ranked low in Table XIV. However, if it is present, then it becomes a much more important property that must be properly assessed. In view of its virtually negligible probability of occurrence in the wastes to be treated by the techniques described herein and its high weighting factor when present, it is included but deemed essentially unimportant for the purposes of the search for alternative baseline waste-form technologies.

This list is extensive. When used to aid the process by which the degree of suitability for a specified waste form can be assessed, the contents of Table XIV elucidate the minimum number of issues and measurements that must be considered: that is, these properties can be assigned rankings that, when applied to an individual waste-form technology, produce a numerical guide that indexes the suitability of the waste form. Alternatively, the rankings can be used in order to assess the relative suitabilities of various waste applications for a single waste-form technology.

The first approach is advocated herein because the numerous types of waste that must be treated under the auspices of the DDT&E Program (Table VI) vary considerably in properties. The format provided in Table XV is one application of the approach just described.

The literature search that underpins this report revealed that the information which is needed in order to complete the form in Table XV is largely unavailable, even for a single type of waste. Quite detailed investigations have been reported for either individual technologies or individual waste streams, as the preceding section (Sect. 6) has revealed. However, these reports do not generally provide sufficient information that permits even a small subset of the criteria in this table to be analyzed for the candidate alternative waste forms to grout and glass.

Often, apparently contradictory and irreproducible claims accompany the descriptions of the most developed technologies. For example, those for sulfur-polymer cement and the various organic thermosets and thermoplastics rarely pertain to similar wastes and tend to emphasize the technology rather than the aspects of the waste that would justify attempts to compare different sets of data. The descriptions for the less developed technologies, such as those for glass-ceramics and ceramics, reveal that these waste forms are at the laboratory scale. This status implies that comparisons beyond those of scale (i.e., the criterion of utilization experience in Tables XIV and XV) and those regarding the

technical aspects of the chemistries, the processing techniques, the microstructural features, and the various manifestations of these in the properties of the waste-form matrices remain unconfirmed and are largely unjustified.

The literature search and the information in preceding sections of this report lead to two important conclusions regarding the ability to address the criteria in Table XIV, so that the different types of waste-form matrices can be compared, for example, via the form in Table XV. First, the nonuniform character of the waste streams investigated makes the comparison of competing technologies difficult at best and fraught with unpredictable consequences when these are applied to newly encountered wastes. Simply, more must be known about the combinations of waste and waste-form matrix that fail, as well as those that succeed, at meeting regulatory requirements and displaying other desirable properties. Second, the general lack of experimental controls in the documentation that promotes individual technologies greatly reduces the ability to project the success with which an individual waste-form technology can be extended to other wastes and various engineering limitations. This aspect reveals that the field of S/S for hazardous wastes has been evolving in a somewhat haphazard manner.

Some recent publications on the nature of hazardous wastes and the environmental issues pertaining to them [148,153,156,162,163,167] and the science and technology of stabilization and solidification of hazardous wastes [275,281,282,283] indicate that this evolution requires more systematic studies in order for the field of hazardous-waste stabilization and solidification to progress. An increased emphasis on these topics is needed. Research standards by which the criteria in Table XIV can be investigated and compared for different waste-form technologies, akin to those which evolved for the S/S of radioactive wastes [272], must be developed for the S/S of hazardous wastes. Both applied and fundamental studies of the scientific and engineering aspects are compulsory.

The status of S/S technology for mixed wastes has evolved to an even lesser degree, possibly because its classification as such is quite recent. As information emerges from hazardous-waste studies, mixed wastes should be less problematic than they are now.

8. CONCLUSIONS AND RECOMMENDATIONS

8.1. General Approach

Grout and glass waste forms represent the two baseline technologies that constitute the forefront of the stabilization and solidification (S/S) of hazardous, radioactive, and mixed wastes. Grout has been successfully used to treat many waste streams. Glass has been largely applied to problems regarding radioactive wastes, but its adaptation to hazardous and mixed wastes has great potential.

Some types of wastes, notably the RCRA metals, can present problems for grout and glass and their respective technologies. These problems can be acute in the case of mixed, hazardous, and radioactive wastes. Moreover, some problematic wastes are not likely to be readily immobilized in grout or glass in a fashion that permits the standards set by the regulatory requirements and other nonregulated, desirable performance criteria. Many of these wastes are of particular concern for the DDT&E Program, and they are summarized in Sects. 4 and 6.1. The essential hazardous features of these wastes, their physical formulation, and their relative abundancies are presented in Tables III, IV, and VI, respectively.

A literature search and a comprehensive survey were undertaken in order to identify candidate alternative baseline technologies and to assess them. The various sources used for information are outlined in Table II. The technical applicability and present suitability for implementation of the candidate alternatives formed the bases by which the viability of each candidate was assessed. The candidate waste forms were classified according to their general, materials-oriented composition. Six generic waste-form categories were identified, and relevant information was retrieved and compiled on each. They are inorganic matrices, organic thermosets, organic thermoplastics, vitrified matrices, devitrified matrices, ceramics, and metallic matrices. The general advantages and disadvantages of these materials are summarized in Table VII.

These categories were addressed by identifying and understanding the nature of each type of waste-free matrix. The major areas of concern were the raw materials or starting components that are typically used to fabricate each type of material, the basic chemistry and physics of major processing schemes by which each is made, the common compositional and processing variants within each family, and the inherent properties that each type of matrix possesses.

An important tenet that was invoked in order to identify and to assess candidate waste forms is that the overall behavior of the waste-containing matrix is an accumulation of properties that derive from the individual waste species that survive the processing stages, the host material, and any new phases that result from the chemical and physical interactions between the waste residue and the matrix. Consequently, descriptions of the various wastes considered in the DDT&E Program are relevant to the present effort and were, therefore, developed. From these, representative problematic cases were drawn upon, as needed, in order to place a perspective on the technical viability of each type of waste-form technology considered.

Some general constraints were applied in these efforts, when possible. These are outlined in Table I. Although they proved to be helpful guidelines, they were inadequate for the full assessment of the broad range of waste-form technologies. Hence, a more complete set of criteria was established. The properties that constitute this set are discussed in Sect. 7 and are summarized in Table XIV. Many can be used in order to assess the individual waste forms and to facilitate comparisons among the various waste-form technologies.

Unfortunately, the literature search revealed that the requisite information for a systematic assessment of the individual technologies and extensive comparisons among the different ones is unavailable in the technical literature. Consequently, the criteria in Table XIV remain at the present time as qualitative guides around which useful discussion is possible. As future information is gathered, as described in Sect. 7, the properties listed in Table XIV can be applied and updated. A fundamental finding of the research conducted for this report is that the iterative effort just proffered, namely, to update routinely the measures by which acceptable performance is distinguished from unacceptable characterizations, is crucial for the development of waste-form technology. This theme underpins and permeates the report.

Summarily, this status necessitated the use of identifiable technical criteria by which the various waste-form technologies can be assessed: that is, the materials-oriented properties of the waste forms became paramount in the execution of the assessment process.

8.2. General Findings

A critical and inescapable conclusion of the information summarized in Sects. 3 and 4 is that the microstructure of the final waste-matrix system sets the degree of success with which the regulatory

requirements and other nonregulated desirable standards are ultimately met by an individual waste-form technology. Stated alternatively, the composition, the principal physical phases, the degrees of crystallinity, the types and amounts of porosity, the grain sizes and grain-size distributions, the grain morphology, and the nature of intergranular phases, among other features, combine to determine the properties that the waste form exhibits. Depending upon the specific manner by which the final waste forms are examined in practice, various subsets of properties provide the behavior observed. Upon reflection, this set of concepts seems obvious. Still, they cannot be understated. The principle that the microstructure governs whether or not a waste form exhibits acceptable properties underscores each S/S technology. The success with which the microstructure is controlled and the flexibility by which it can be altered establish, in turn, the relative attractiveness of an individual S/S technology.

The central technical conclusion just stated is discussed in Sect. 5. It leads to the second, more specific conclusion that has far-reaching implications: namely, the relationships among (1) the chemistry (i.e., the composition and reactivity of both the waste and the host material); (2) the processing history; (3) the microstructure of the combined, fabricated system; and (4) the properties that this final system displays govern the overall waste-matrix behavior. None of these aspects can be considered or altered independently of the others without introducing two significantly detrimental consequences: a biased assessment of the candidate waste forms, and the generation of error-prone predictions regarding their performances. The severity of the bias and the magnitude of the errors depend, of course, on the sensitivity of the combined waste-matrix system to the specific aspects that are neglected and to the parameters that are altered.

These concepts constitute an explicit statement of an apparently new operating paradigm that focuses on the interrelationships just cited. It has proven to be useful during the course of the assessment of materials and technologies reported herein, by specifically permitting the resolution of obstacles that stemmed from a lack of detailed information. This paradigm directly addresses both the technical aspects of the waste forms and our perceptions of the viability and suitability of each one. Further, two interrelated findings emerged for grout and glass, based on the paradigm: (1) much of the success of grout-based waste-form technology and the potential of glass-based waste forms are consequences of the ability to manipulate the microstructure of these waste forms, and, in turn, (2) this ability for microstructural tailoring comprises the control of the composition and the processing parameters. Sometimes, this view has been explicitly recognized and incorporated during waste-form development, whereas at other times it emerges as an afterthought of the technical state of the art for each of these materials and technologies. The development of newer and

advanced waste forms and their accompanying technologies will be accelerated and optimized if the core interrelationships for each waste-form technology are clarified and used as a basis for improvements.

Clearly, the microstructure of the final waste form is key to the tailoring of its properties and to the ultimate ability to meet the regulatory and other desirable criteria. This conclusion and its supporting concepts lead, in turn, to an understanding of two common observations: the ability of chemically stabilized waste species to migrate out of the host matrix generally differs from that of the corresponding encapsulated forms under the same external conditions, and the degree of subdivision of encapsulated waste and the degree of homogeneity with which it is distributed throughout the host matrix greatly contribute to the ability of that waste to be liberated or to migrate out.

8.3. Specific Conclusions Regarding Waste-Form Suitability

The research conducted for the assessment process comprised an extensive literature search and survey. Six categories of materials were examined in detail. These are inorganic matrices, organic thermosets, organic thermoplastics, devitrified matrices, ceramics, and metallic matrices. The primary materials within each family and the main features are summarized in Table XVI.

8.3.1. Alternative Baseline Technologies

Inorganic Waste Forms. The major inorganic alternatives subjected to the assessment process are gypsum-based matrices and sulfur-polymer cement (SPC). Of these two, SPC is the one which demonstrates the better probability of being adapted for the purposes of the DDT&E Program. SPC is thermoplastic in the molten state; it is crystalline in the solid state. Encapsulation, without extensive chemical stabilization, is the primary mechanism of immobilization and containment for SPC. Consult Sects. 3.1.2, 3.1.3, and 6.2.1 for details on their use as waste forms.

Organic Waste Forms. Urea-formaldehyde (UF) and related condensation resins, epoxy-base polyethers, and unsaturated polyesters are the candidate organic thermosetting materials that were considered. The properties of UF resins represent most of those exhibited by the other materials. The polymers made from these resins consist of cross-linked rigid microstructures that immobilize waste constituents via encapsulation. The generation of water, combined with the necessity for its complete removal, and the limited processing modes

associated with extensively cross-linked matrices are detrimental aspects for these materials. Discussions on the waste-free matrices are in Sects. 3.2.1, 3.2.2, and 3.2.3. The use of these thermosets as waste forms is discussed in Sect. 6.2.2.

Two varieties of organic thermoplastic waste forms were considered. These are bitumen and vinyl based, essentially linear polymers. Bitumen is a colloidal dispersion with a continuous liquid phase, and the suspended solids occupy approximately 60% of the volume and, thereby, impart viscoelastic properties to the system, which are macroscopically classified as thermoplastic behavior. Encapsulation is the mechanism by which bitumen immobilizes waste. Although some cross-linking of the fluid phase molecules is possible and does increase the viscosity of this phase, bitumen retains fluid properties and, therefore, requires secondary containment. Without other support, bitumen will flow and leave the insoluble waste components in a concentrated state. The discussions regarding this material and its use as a waste form appear in Sects. 3.2.4 and 6.2.2, respectively.

Polyethylene is the central material for vinyl-based thermoplastic polymers. Although its polymeric chains can be slightly branched, it is essentially a linear coiled polymer. A wide range of compositional variants exists; these constitute viable alternatives when improved polymer properties are needed. Encapsulation is the primary mechanism by which these materials immobilize waste. Thermoplastic, vinyl-based polymers offer great flexibility in processing. Small degrees of crystallinity may be used to advantage in further restricting the mobility of encapsulated waste species; however, this concept seems to have not been explored directly. The discussions regarding polyethylene, its vinyl-based cousins, and the uses of these materials as waste forms appear in Sects. 3.2.5 and 6.2.2, respectively.

Devitrified Waste Forms. Glass-ceramics are the materials emphasized in this category. These materials are prepared by making a precursor glass that contains all components that are desired in the final component. This glass is annealed in order to induce crystallization controllably. Ultimately, nearly 98% of the material is crystalline ceramic, and the remainder is a residual glassy phase.

In a crude sense, the glassy phase can be deemed to cement or bind the ceramic grains. On the microstructural level, the glassy phase imparts properties to the composite system that the ceramic phases do not possess. The great reduction in brittleness that typifies glass-ceramics (i.e., when compared with the corresponding ceramic materials) is one notable feature that the glass phase ensures. Being ceramic in detail, glass-ceramics

can be made to be very stable thermodynamically. The central compositions are silicate-based, and aluminosilicates look promising for the long-term immobilization of hazardous, radioactive, and mixed wastes.

Although encapsulation is the predominant mechanism of immobilization, chemical stabilization is possible, and it can occur in either the glassy phase (albeit the minor phase), the ceramic phase, or both. These materials are essentially unexplored for uses in waste-disposal technology for hazardous and mixed wastes. They have been investigated for application of high-level radioactive wastes. Descriptions of these materials and their use as waste forms are in Sects. 3.4 and 6.2.4, respectively.

Ceramic Waste Forms. These materials can have a wide variety of compositions, and some of these have demonstrated technical superiority regarding their use as waste forms for high-level radioactive wastes. In many instances, they perform better than borosilicate glass does. Little has been done, however, to extend the superior properties just mentioned to the resolution of waste-immobilization problems of hazardous and mixed wastes. Ceramic forms are clearly the most stable for many of the hazardous metals. The prevalence of natural minerals that contain these very elements affirms this point. Also, the desirability of transforming hazardous waste species into ceramic forms via various treatment strategies supports this view. Nonetheless, the breadth of compositions that makes ceramics attractive can be a daunting obstacle to the thermodynamics-based immobilization of wastes.

Fortunately, encapsulation in a dense ceramic waste form essentially ensures immobilization in most cases. Such a state suggests the need for geologic duration in order for the waste species to migrate out of the waste form, even in the event that the conditions are not the most stable. The very low diffusivity properties of ceramics underpins this degree of metastability, indicating geologic times for diffusion (leaching) that well exceed the 300-year target [358].

The most reasonable compositions for the application of ceramic waste forms are based on alumina (Al_2O_3) and silica (SiO_2). These can be formulated and processed, via a variety of processing and heat treatment techniques, in order to generate aluminosilicates and composites of mixed phases. Hence, encapsulation is the primary mechanism for the full range of hazardous and radioactive species of concern in the DDT&E Program. However, research on the immobilization of high-level radioactive wastes suggests that optimized

chemical stabilization is possible for the most troublesome hazardous species. The descriptions of the waste-free materials and their uses as waste forms appear in Sects. 3.5 and 6.2.5.

Metallic Waste Forms. These are composite systems in most cases, and the metallic phase acts as a secondary encapsulation medium. In some other cases, the preparation of an alloy that contains hazardous metals among the more prevalent matrix metals, such as copper, constitutes a waste treatment, rather than a waste-form technology. Consequently, metallic matrices are not considered viable candidates as alternatives to grout and glass. Consult Sects. 3.6 and 6.2.6 for details.

Baseline Technology. The overriding conclusion of this effort is that no baseline technology currently exists that can be implemented immediately as an alternative to grout-based and glass-based technologies. A number of restrictions either limit or preclude the implementation of each one considered. The technologies that are most developed focus on thermoplastic and thermosetting media. The former is favored here, owing to the ease of processing and the requisite flexibility to tailor the microstructure.

The thermoplastic materials—sulfur-polymer cement (SPC), bitumen, and polyethylene—represent the waste-form technologies that are most developed. These have quite distinct microstructures, as the summary in Table XVI emphasizes. None interacts with the majority of hazardous and radioactive wastes encountered in the DDT&E Program. This lack of interaction makes them suitable and flexible for the purposes of encapsulation.

Each warrants further study. This effort should emphasize the short-term development in each case, particularly the ability to meet engineering criteria. Each has attractive features that can dominate in the final assessment.

SPC possesses a crystalline microstructure that resembles naturally occurring sulfur. Hence, the encapsulation-derived benefits cited earlier for ceramics may be also possible with the encapsulation in SPC. However, considerable efforts still need to be made in examining the broad range of wastes that must be addressed in the DDT&E Program.

The encapsulation of waste in bitumen has two main technical benefits. It is an easily processed material, and it adheres to most surfaces sufficiently well that, although it may not wet inorganic waste particulates,

high waste loadings are still possible. Significant limitations include its dispersion-based microstructure, its permeability by gases, and its impermeability to entrapped liquid water that, ultimately, can lead to osmotic swelling. Each of these limitations demands secondary containment.

Thermoplastics, such as polyethylene, exhibit important features that warrant serious consideration. The microstructurally related ones derive from the fact that various densities, degrees of crystallinity, and comonomers lead to a flexibility that is unmatched with most other waste forms. This advantage is strengthened by the variety of processing techniques that are available. Unfortunately, the microstructural features of polyethylene and its vinyl-based relatives have not been seriously examined regarding the immobilization of hazardous and radioactive wastes. The lack of interaction between the matrix and waste species ought to be adjustable, at least to some extent. The vinyl-based polymers are also susceptible to osmotic swelling. However, their chains can be cross-linked in order to improve the strength and the resistance to the deleterious effects derived from this swelling.

None of these individual waste-form technologies is sufficiently developed at the present time to be deemed at the baseline scale. The selection of a best waste form depends, to a great extent, on the specific wastes and their physicochemical characteristics. In view of these facts, the ranking sequence of these thermoplastic matrices is SPC > polyethylene >> bitumen. This sequence is based on the materials-oriented criteria, as explained earlier in this section and in Sect. 7.

SPC is selected as the primary alternative for short-term encapsulation studies. The crystallinity and the similarity of its composition and structure to those found in natural sulfur deposits [294,297,315] supersede the advantages of polyethylene and bitumen.

8.3.2. Best Immobilization Technology

The selection of sulfur-polymer cement (SPC) is based on its potential to provide the minimum loss of hazardous and radioactive waste species from a thermoplastic medium. However, this material does not represent the best immobilization attainable. Another alternative is needed. Ideally, a suite of alternatives is needed because the selection of best waste form is waste driven.

Better Alternatives. Among the remaining candidates, the families of glass-ceramics and ceramics are superior. They have identifiable traits that have been shown to outperform glass for the immobilization of high-level wastes. Similar advantages should emerge, after careful research is conducted, regarding the immobilization of the RCRA metals. These metals, their compounds, and waste residue from the treatment of organic wastes are predominantly inorganic. Hence, the thermoplastic materials just reviewed are very much unlike the wastes in most respects. Although SPC is essentially inorganic, its microstructure precludes the extensive interactions that underpin chemical fixation.

Clearly, ceramic waste forms resemble the inorganic waste most. Therefore, the driving forces that cause waste species to be liberated from a host matrix are significantly reduced in ceramic matrices. Nature provides such containment in the form of minerals. These are largely either crystalline or glassy. Importantly, most are stable, even in the presence of water.

In view of the greater stability found in the family of ceramics, these must be considered among the most desirable waste forms for long-term stabilization. The broad range of ceramic matrices that have been examined as potential waste forms for high-level waste [98,271,272] demonstrates that some of these waste forms may be increasingly suitable for hazardous and mixed wastes, as the economic, social, technical, and regulatory requirements evolve toward a more restrictive set of limitations, while reflecting a comprehensive set of environmental goals [156,165].

Glass-ceramics offer essentially the same degree of stability and exhibit the additional feature that the processing can be tailored, in principle, in order to optimize the distribution of chemically stabilized species in the glassy phase, the ceramic phases, or both. Furthermore, the nucleation of ceramic phase that encapsulates waste particulates would ensure *in situ* secondary encapsulation on a microscopic scale.

These considerations lead to the recommendation that glass-ceramics be examined as a long-term solution for the chemical stabilization and encapsulation of hazardous, radioactive, and mixed wastes. Data on waste-containing glass-ceramics are presently unavailable. Nonetheless, the fabrication of glass-ceramics can be viewed, at one level, as an outgrowth of vitrification technology. An important distinction is stressed at this point. The precursor glass for the glass-ceramic waste form must be made in such a fashion that it can be controllably altered during the annealing stages and that the final two-phase system exhibits the desired

properties. Based on the proliferation of oxygen, silicon, and aluminum in nature, glass-ceramics that are based on silica (SiO_2) and alumina (Al_2O_3) might be assigned first priority.

Closing Remarks. The foregoing considerations lead to the possibility that no single waste form is likely to be suitable for each type of waste. Three important implications follow from this concept: (1) the chemical and physical properties of each hazardous waste stream establish the technical requirements of acceptable candidate waste forms; (2) the properties of the candidate waste forms, in turn, set the relative priority that should be associated with each potential waste form; and (3) the issues of cost only apply to those waste forms that survive the assignment of technical priorities for each type of waste. The last implication follows from the regulatory requirements that each type of waste must be treated for disposal and that only those wastes for which no acceptable incineration, stabilization, and solidification technology exists may be stored.

The paucity of reliable data on the use of the various alternative waste-form technologies for hazardous and mixed wastes underscores a clear need for applied and basic research. The advocacy of sulfur-polymer cement (SPC) is made in full recognition that microstructural studies and related investigations must be conducted, in addition to studies regarding the production of this waste form and the ensuing encapsulation of waste components. The recommendation that glass-ceramics be pursued for the long-term immobilization needs is clearly based on the faith that scientific and engineering research on these materials will provide guidelines for further development. Attention to the paradigm that emerged from the present study must accompany the research and development of both SPC and glass-ceramics.

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11. GLOSSARY: IMPORTANT SYMBOLS, TERMS, AND NOMENCLATURE [338-370]

11.1. Symbols

ALARA	As low as reasonably achievable
BDAT	Best demonstrated available technology
C ₂ S	Dicalcium silicate, 2CaO·SiO ₂
C ₃ A	Tricalcium aluminate, 3CaO·Al ₂ O ₃
C ₃ S	Tricalcium silicate, 3CaO·SiO ₂
C ₄ AF	Tetracalcium aluminoferrite, 4CaO·Al ₂ O ₃ ·Fe ₂ O ₃
CAA	Clean Air Act, 1967 [338,342]; also known as the Air Quality Act
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act; Superfund, 1980 [343,344,345,346]
CFR	Code of Federal Regulations [348]
CFS	Chemical fixation and solidification
CWA	Clean Water Act, 1977 [341]
DDT&E	Development, Demonstration, Test and Evaluation (Program) [325]
DOE	U.S. Department of Energy
DOT	U.S. Department of Transportation
EDS	Engineering Development Section, Chemical Technology Division, Oak Ridge National Laboratory
EPA	U.S. Environmental Protection Agency
FFCA	Federal Facilities Compliance Agreement, 1992
FFCAct	Federal Facilities Compliance Act, 1992 [347]
FFCA/DDT&E	Subsets of the DDT&E that focus on FFCA
FWF	Final waste form
HDPE	High-density polyethylene
HLW	High-level waste
HSWA	Amendments to RCRA, 1984 [362]
IAEA	International Atomic Energy Agency
ILW	Intermediate-level waste
LDPE	Low-density polyethylene
LDR	Land Disposal Restrictions

LLDPE	Linear low-density polyethylene
LLW	Low-level waste
LMES	Lockheed Martin Energy Systems, Inc.
MWIR	Mixed Waste Inventory and Repository Program
MWTF	Mixed Waste Treatment Facility [326]
NPDES	National Pollutant Discharge Elimination System [341]
NRC	U.S. Nuclear Regulatory Commission
ORR	Oak Ridge Reservation
OSHA	Occupational Safety and Health Act, 1970 [339]
PC	Portland cement
PE	Polyethylene
POTW	Publicly Owned Treatment Works [363]
RCRA	Resource Conservation and Recovery Act, 1976 [360,363,364]
S/S	Stabilization/solidification
SARA	Superfund Amendment and Reauthorization Act, 1986 [343,344,345,346]
SLLW	Solid low-level waste
SPC	Sulfur-polymer cement
Synroc	Synthetic rock
SWSA	Solid Waste Storage Area
TCLP	Toxicity Characteristic Leach Procedure
TRU	Transuranic waste
TSCA	Toxic Substances Control Act, 1976 [340]
TSD	Treatment, storage, and disposal
UF	Urea-formaldehyde

11.2. Terms and Nomenclature

Admixture	A material added in small quantities to a batch in order to alter the working or performance characteristics of the batch
Aggregate	An inert material, such as sand, gravel, slag, shell, or broken stone, which is to be mixed with cement in order to form concrete or mortar

Asphalt	A bitumen that is manufactured via distillation from petroleum and related materials
Asphaltene	Any of the dark, solid constituents of crude oils and the very high-molecular-weight polar species in other bitumens that are soluble in carbon disulfide but insoluble in paraffin naphthas; asphaltene holds most of the organic constituents in bitumen
Basalt	(1) Fine-grained igneous rock that is primarily composed of calcium-rich plagioclase feldspar and pyroxene, but may also contain other materials such as olivine, magnetite, and apatite [359]; (2) the most common type of rock formed from molten volcanic lava [261,359]
Binder	The main component of a solidification formulation, which binds or cements together the components of the waste into a solid mass (e.g., portland cement, bitumen, and organic polymers)
Biodegradation	The physical or chemical breakdown by microorganisms
Bitumen	(1) Any of a wide variety of hydrocarbons with high molecular weight, obtained naturally (e.g., asphalt or tar) or by distillation from coal and petroleum, whose two major components are asphaltene and malthe compounds (asphaltene compounds give bitumen colloidal properties, and malthe compounds impart it with viscous liquid properties [359]); (2) a native asphalt; (3) a thermoplastic organic material that is composed of a wide variety of mixtures of high-molecular-weight hydrocarbons that are soluble in carbon disulfide; the characteristics of bitumen may classify it as a semisolid or a solid because of its viscoelastic characteristics; (4) a naturally occurring viscous hydrocarbon having a viscosity at ambient (deposit) temperature and a density at 15.6° C that exceed 10 Pa·s and 1000 kg m ⁻³ , respectively [352]
Bulking agent	An addition that primarily adds to the total solids and viscosity of a waste, thus preventing settling out of the suspended waste components before solidification can occur; it may also help produce a solid with improved physical properties; two types of bulking agents are those that are essentially inert in the system and those that also have reactive capacity or pozzolanic activity [102]
Calcination	(1) Heat treatment, often under oxidizing conditions, at high temperature without fusion so that hydrates, carbonates, and other compounds are decomposed and the volatile material is expelled; (2) a process that involves the evaporation of a waste solution to sufficient dryness and the heating of the residue in air, so as to convert the metal-containing constituents to oxides
Calcine	A material or mixture of materials that has been heated to high temperature, but without fusion, to eliminate volatile constituents and to produce desired physical changes

Cement	A powder produced from a calcined clay-limestone mixture which is the bonding medium in mortar and concrete and, when mixed with water, forms a paste that hardens into a stone-like mass
Cementation	The setting of a plastic material
Ceramic ²³	Any of a class of inorganic, nonmetallic products which are subjected to a temperature of at least 540°C during manufacture or use, including metallic oxides, borides, carbides, and nitrides, and mixtures or compounds of such materials
Characterization	Those features of the composition and structure, including defects, of a material that are significant for a particular preparation, study of properties, or use and suffice for the reproduction of the material; normative characterizations include (a) microstructure (e.g., obtained from optical, scanning electron microscopic, electron probe, and similar analyses), (b) crystallographic or atomic structure (e.g., obtained from scanning transmission electron microscopic, x-ray and electron diffraction techniques), and (c) bulk chemical composition [367]
Chemical fixation	Stabilization
Closure	The act of securing a hazardous waste management facility pursuant to the requirements of Ref. [348i]
Colloid	A substance, usually a solid, in the form of submicroscopic particles, typically in the range 1 to 1000 nm, that do not settle out when in suspension (e.g., dispersed material in a two-phase system) or solution (viz., macromolecules)
Colloidal system	An intimate mixture of two substances, one of which, the dispersed phase (colloid), is uniformly distributed in a finely divided state throughout a second substance, the dispersion (dispersing) medium; the dispersion medium or dispersed phase may be gas, liquid, or solid; also known as a colloidal dispersion or colloidal suspension
Composite	A combination of two or more (organic, inorganic, or metallic) materials, present as separate phases and combined to form desired structures, so as to take advantage of certain desirable properties of each component
Concrete	A homogeneous mixture of portland cement, aggregates, and water; also may contain selected admixtures

²³This term is used herein to designate crystalline materials that are usually polycrystalline and polyphasic, unless stated otherwise. [99,408]

Corrosive	The characteristic category for (a) an aqueous solid waste with a pH less than 2 or greater than 12.5 or (b) a liquid waste that corrodes steel (SAE 1020) at a rate exceeding 6.35 mm year ⁻¹ at 55° C
Curing	(1) The process by which the properties of a resin material are changed via polymerization (i.e., chemical polycondensation or addition reactions), in which a soft gel forms first, followed by a second stage in which polymerization is rapid; (2) the process by which concrete is kept moist in order to provide sufficient water for the cement to harden
Devitrification	The formation of crystalline structures in a glassy matrix, such as may occur in a glass, glaze, or porcelain enamel during the cooling of a vitreous mass
Devitrified glass	A glass that has been converted from a conventional vitreous state to a crystalline state, often by means of a nucleating agent incorporated in the original batch; nucleated crystals are precipitated and grow when the formed and finished item is subjected to subsequent controlled heat treatment; such a glass is strong and highly resistant to thermal shock.
Disposal	The discharge, deposit, injection, dumping, spilling, leaking, or placing of any solid waste or hazardous waste into or on any land or water so that such solid waste or hazardous waste or any constituent thereof may enter the environment or be emitted into the air or discharged into any waters, including groundwater
Disposal facility	A facility, or part of a facility, where hazardous waste is intentionally placed into or on the land or water and will remain after closure
Embedment	Enclosure of hazardous, radioactive, or mixed waste in a solid waste form such that the waste exists as macroscopic particulates and solids embedded in a solid waste-form matrix
Emulsion	A dispersion of droplets of one liquid in another, immiscible liquid; the size of droplets may be on the macroscopic or microscopic scale
Encapsulation	Enclosure of hazardous, radioactive, or mixed waste in a solid waste form such that the waste exists as (a) microscopic particulates (microencapsulation), (b) particulates contained within or coated with an impervious layer that is distinct from the matrix material (macroencapsulation), or (c) macroscopic particulates and solids embedded in a solid waste form matrix (embedment)
Final waste form ²⁴	(1) A liquid-free solid matrix that is used to stabilize or to solidify hazardous, radioactive, or mixed waste; (2) the physical and chemical form of the waste material without its packaging [358,359]

²⁴Interchangeable in this report with the term *Waste form*.

Flux	Any substance that promotes the fusion and flow of a ceramic or glass mixture when subjected to heat
Fly ash	Fine particles of matter in flue gases, usually resulting from the combustion of fossil fuels; sometimes used as a pozzolan or as a filler in some cements
Fusion	(1) The process of melting, frequently with interaction of two or more materials, to form a more or less homogeneous mass; (2) the joining by the use of heat
Gel point	The point at which a solution or slurry begins to increase in viscosity and exhibits elastic properties
Gel	(1) A two-phase colloidal system consisting of a solid and a liquid in more solid-like form than a sol; (2) a suspension (e.g., an aqueous clay suspension) or polymer solution that behaves as an elastic solid rather than a liquid.
Gelation	Formation of a gel from a sol
Generator	Any person, by site location, whose act or process produces "hazardous waste" as identified in [348j]
Glass	Any of a large class of amorphous, rigid, inorganic, nonmetallic materials of widely variable compositions, mechanical properties, and optical characteristics that solidify from the molten state, usually without crystallization; typically, the compositions include silica, boric acid, alumina, basic oxides of sodium, potassium, or other such ingredients; the products may be transparent, translucent, or opaque, colorless, or in a wide variety of colors, and often are regarded as supercooled liquids rather than true solids; two important distinguishing aspects of glasses that make them unique among the generic class of ceramics are their noncrystallinity and their derivation from the liquid phase [99,443]
Glass-ceramic	A predominantly crystalline product produced by the controlled crystallization of glass, often induced by heating; characterized by low-thermal expansion and high thermal shock resistance
Glass transition	The change in an amorphous region of a partially crystalline polymer from a viscous or elastic (rubbery) condition to a hard, relatively brittle, and inelastic one, usually brought on by a change in temperature
Grout	A mixture of portland cement and water that does not contain aggregates [359]; admixtures are often used to improve properties, such as the ability to flow, to aid or to supply additional cementitious reactions, or to act as fillers
Hazardous waste	(1) A waste, or combination of wastes, which because of its quantity, concentration, toxicity, corrosiveness, mutagenicity, flammability, or physical, chemical, or infectious characteristics may (a) cause or significantly contribute

to an increase in mortality or an increase in serious, irreversible, or incapacitating reversible illness; or (b) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, buried, or otherwise managed [348k]; (2) generally, hazardous waste (a) is not degradable and persists in natural environments, (b) can be magnified biologically, producing a much larger hazard, (c) is noxious or toxic, and (d) may cause detrimental cumulative effects

High-level waste	(1) A highly radioactive fission product that is separated during reprocessing from the valuable materials in spent nuclear fuel rods; (2) a long-lived radioactive waste (i.e., one whose lifetime exceeds 30 years [355,358,359] and that emits a significant amount of heat)
Hydrogeology	The study of the groundwater conditions, especially the properties, distribution, and movement of water in the soil and the underlying rocks [359,261]
Ignitable	The fire-related characteristic category for (a) a liquid, other than an aqueous solution containing less than 24 vol % alcohol, with a flash point below 60°C; (b) nonliquid waste that is capable of causing fire through friction, absorption of moisture, or spontaneous chemical changes, and, when ignited, burns so vigorously and persistently that it creates a hazard under standard temperature and pressure; (c) a compressed gas [348a], or (d) an oxidizer [348b]
Intermediate-level waste ²⁵	A long-lived radioactive waste [355,358,359]
Leachate	Any liquid, including suspended components in a liquid, that has percolated through or drained from hazardous waste
Lime	Calcium oxide (CaO), which is used as a fluxing agent in glass, pottery, glazes, and porcelain enamels, and as a component in portland cement, mortar, and plaster
Low-level waste	(1) For the purpose of the ANSI/ANS-16.1 Standard [368,369], a radioactive waste as defined by Ref. [348c] and [348h] for long-lived and short-lived radionuclides, respectively; waste that contains a low level (or low concentration) of radioactive material, which has a relatively short lifetime (i.e., less than 30 y [355,358,359]); (2) a radioactive waste that does not require shielding and cooling [354]
Macroencapsulation	Enclosure of hazardous, radioactive, or mixed waste in a solid waste form such that the waste exists as particulates contained within or coated with an impervious layer that is distinct from the matrix material

²⁵ This term, defined by the International Atomic Energy Agency (IAEA), is not typically used in the United States, although it is a member of the IAEA. Apparently, this waste is classified in the United States as a high-level waste.

Matrix	The continuous, solid matter within which aggregates or crystals are embedded or bonded
Micelle	An aggregate of surfactant (i.e., a substance that lowers the surface or interfacial tension of the medium in which it is dissolved) molecules or ions that forms spontaneously at a sufficiently high concentration of the surfactant; micelles contain from tens to hundreds of molecules or ions; salts of fatty acids that contain at least eight carbon atoms are common surfactants that form micelles at concentrations that exceed a critical value that depends on the molecular architecture
Microencapsulation	Enclosure of hazardous, radioactive, or mixed waste in a solid waste form such that the waste exists as microscopic particulates
Mineral	A naturally occurring substance with a characteristic chemical composition expressed by a chemical formula, typically required to be of inorganic origin and crystalline structure
Mixed waste	(1) A waste that either exhibits both hazardous and radioactive properties or is otherwise classified as hazardous and radioactive; (2) a solid waste that is contaminated with radioisotopes, possibly containing fissile-mixed, low-level mixed, or TRU-mixed waste in combination with hazardous materials, as defined under RCRA and related statutes [322]
Mullite	An orthorhombic, crystalline aluminum silicate with the formula $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$.
Neutralization	Reduction of the excess acidity or basicity in a waste by the addition of base or acid, respectively, or by dilution, in order to achieve an aqueous pH in the range 2 to 12.5
Polymerization	(1) The bonding of two or more monomers in the production of a polymer; (2) any chemical reaction that produces such bonding; polymerization occurs by (a) condensation reactions, such as those that produce water or hydrochloric acid as by-products; and (b) addition reactions, such as those involving vinyl monomers for which at least one unsaturated carbon-carbon bond (i.e., $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ in the case of double and triple bonds, respectively) exists
Portland cement	A hydraulic cement prepared by calcining powdered mixtures of hydraulic calcium silicates, followed by pulverizing the resultant clinker, together with additions of gypsum or other forms of calcium sulfate, to a fine powder
Pozzolan agent	A material such as fly ashes and blast-furnace slags which, in finely divided form, will exhibit cementitious properties when mixed with lime and water
Prepolymer	An intermediate in a polymerization synthesis whose molecular weight is between that of the original monomer (or monomers in the case of a copolymerization process) and that of the final, cured polymer or resin

Primary waste	Unprocessed (raw) waste that is unchanged from the form and quantity in which it was generated [359]
Reactive	The characteristic category of a waste that (a) is normally unstable and readily undergoes violent change without detonating; (b) reacts violently with water; (c) forms potentially explosive mixtures with water; (d) when mixed with water, generates toxic gases, vapors, or fumes, in a quantity sufficient to present a danger to human health or the environment; (e) is capable of detonation or explosive reaction if subjected to a strong initiating source or if heated under confinement; (f) is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure; or (g) is a forbidden explosive [348d-348f]
Refractory	(1) The property of being resistant to high temperatures; (2) an inorganic, nonmetallic material that will withstand high temperatures; such materials are frequently resistant to abrasion, corrosion, pressure, and rapid changes in temperature (e.g., alumina, sillimanite, silicon carbide, zirconium silicate)
Resin	A member of a class of solid or solid-like organic products with no definite melting point; generally, resins have high molecular weights and are polymers of either natural or synthetic origin
Retarder	An admixture to cement mix that delays the setting process without altering the composition or identity of hydration products [22]; the mechanism by which retarders operate principally involves their adsorption on the hydrating cement particles [16,18,19,20,21], but may also involve their complexation with the calcium ions that pass into the aqueous phase as hydration proceeds [30]; their tendency to coagulate the calcium silicate solution [11,12,13]; their ability to limit the solubility of alumina [14,15] or their ability to modify the growth of crystals and the morphology of them [26] so as to foster a heightened barrier to further hydration [29]
Secondary waste	By-product waste from the processing of primary waste [359]
Sintering	The bonding of powdered materials by solid-state reaction at temperatures lower than those required for the formation of a liquid phase
Slag	(1) The partially fused mixture of spilled batch, overflowed glass, breeze coal, and clay from the floor of a pot furnace or glass tank; (2) material formed by the fusion of oxides in a metallurgical process or the fused reaction product between a refractory and a flux; (3) a nonmetallic by-product of steel blast furnaces which is crushed and sized for use as concrete aggregate; (4) an electric furnace by-product in the manufacture of phosphate, which may be used as a source of alumina in the manufacture of glass; (5) a pozzolanic material sometimes used in the production of cement

Sludge	Any solid, semisolid, or liquid waste generated from a municipal, commercial, or industrial waste treatment plant, water supply treatment plant, or air pollution control facility, exclusive of the treated effluent from a wastewater treatment plant
Soil-cement	A thoroughly blended mixture of soil, portland cement, and water that is compacted and cured to form a hardened material
Sol	A colloidal solution consisting of a dispersion medium, which may be gas, liquid, or solid, and the colloidal substance (the dispersed phase), which is distributed throughout the dispersion medium
Sol-gel transition	(1) The transition of a one-phase solution to a two-phase gel such as that observed with polymerization processes that yield "almost infinite" molecules [182] that are dispersed throughout the remaining liquid phase; (2) the transition of a two-phase colloidal suspension, composed of individual particles dispersed throughout a liquid phase (sol), to one in which the suspended particles establish a particulate network, such as those characteristic of a flocculated sol
Solid solution	(1) A homogeneous crystalline phase composed of different groups dissolved in one another either in all proportions or over a limited range of compositions; (2) a crystal structure in which an atom, molecule, or ion is substituted for another atom, molecule, or ion that is chemically different but of similar size and shape
Solid waste	Any discarded material that is (a) abandoned (i.e., destined to be ultimately treated for disposal or burned) or (b) accumulated, stored, or treated prior to recycling
Solidification	The conversion of a fluid waste by encapsulation into a monolithic solid of high structural integrity, typically accomplished by the addition of an agent or binder
Sorbent	A material that is used to soak up free liquids by adsorption or absorption
Sorption	The fixation of ions at fluid-solid interfaces via physical phenomena such as adsorption, cation exchange, and isomorphic substitution [261]
Spinel	A group of minerals of the general formula, AB_2O_4 , in which A is a divalent metal or mixture of divalent metals such as magnesium, ferrous ion, zinc, manganese, cobalt, calcium, copper, barium, nickel, and strontium, and B is a trivalent metal such as aluminum, ferric ion, and chromium; spinels are used in the manufacture of ceramic colors and refractories
Stabilization	(1) The reduction of the hazard potential of a waste by converting the contaminants into their least soluble, mobile, or toxic form; (2) chemical fixation
Storage	The holding of hazardous waste for a temporary period, at the end of which the waste is treated, buried, or stored elsewhere

Syneresis	The spontaneous separation of a liquid from a gel or colloidal suspension due to contraction of the gel
Synroc	(1) Synthetic rock; (2) a titanate-based ceramic, whose principal phases of interest are perovskite (CaTiO_3), zirconolite ($\text{CaZrTi}_2\text{O}_7$), and hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$) [410], intended for the immobilization of commercial reactor waste [402,401]
Thermal shock	Exposure of a body or coating to sudden and severe changes in temperature
Thermoplastic	(1) A material that softens when heated and hardens when cooled without change in properties; (2) a physically cross-linked polymer
Thermosetting	(1) The characteristic of a material whose chemically cross-linked molecular structure is responsible for its mechanical properties; (2) the property of a plastic resin that solidifies when heated under pressure, and which cannot be remelted or remolded without destroying its original characteristics, exemplified by epoxies, malamines, phenolics, and ureas
Toxic	The characteristic category for waste whose extract contains any of the contaminants identified by EPA at concentrations equaling or exceeding the maximum values permitted by EPA
Transuranic waste	A waste that contains more than a specific concentration of alpha-emitting isotopes of elements with higher atomic number than 92, the atomic number of uranium
Treatability study	A study in which hazardous waste is subjected to a treatment process to determine (a) whether the waste is amenable to the treatment process, (b) what pretreatment is required, (c) the optimal process conditions needed to achieve the desired treatment, (d) the efficiency of a treatment process for a specific waste, or (e) the characteristics and volumes of residuals from a particular treatment process
Treatment	Any method, technique, or process that is designed to change the physical, chemical, or biological character or composition of a hazardous waste, so as (a) to neutralize the waste, (b) to recover energy or material resources from the waste, (c) to render the waste nonhazardous or less hazardous (i.e., to make it safer for transport, storage, or disposal), amenable for storage, or reduced in volume
Unprocessed waste	Primary (raw) waste that is unchanged from the form and quantity in which it was generated [359]
Vitrification	(1) The progressive reduction in the porosity of a body as a result of heat treatment and fusion during which a glassy or noncrystalline material is formed; (2) the process of incorporating waste into a glass or a glass-like form

Vitrification range	The interval between the temperature at which a body or substance first begins to fuse and the temperature at which the body begins to deform due to melting
Waste	(1) A discarded material; (2) unprocessed, primary, or secondary waste
Waste analysis	(1) The identification of the physical and chemical characteristics of a waste stream, including its weight, volume, radionuclide content, and concentration [322]; (2) waste characterization
Waste form ²⁶	The physical and chemical form of a waste-containing solid product after treatment or conditioning but prior to packaging
Waste package	The waste form plus any container or sum of containers that are required for the handling, transport, treatment, conditioning, storage, or disposal of the waste [358,359]
Waste packet	An individually wrapped and numbered bundle or bag of solid low-level waste [322]
Waste treatment	Any process method that modifies the chemical, biological, or physical character or composition of a waste
Water table	The level of the earth's crust below which rocks and other materials are completely saturated with water [261]

²⁶ Interchangeable in this report with the term *Final waste form*.

TABLES

TABLES

Table I. Pertinent constraints for candidate final waste-form technologies

Constraint	Comments
Compliance is required	Must meet all applicable federal and state regulations
Scale of process is important	High-volume capabilities are preferred
Health and safety issues are to be minimized	Recommended technologies would have a minimum of issues associated with them
Flexibility in the type of waste	Final waste forms that permit the treatment of numerous waste types are preferred
Stabilization dominates solidification	Processes and waste forms that capitalize on stabilization and solidification are preferred to those that solely involve encapsulation as the mechanism by which waste is solidified

Table II. Representative sources consulted

Source	Comments
Recent updates to LMES programmatic goals and regulatory requirements	See Refs. [266], [325], [326], and [337] for programmatic updates and Refs. [363] and [364] for recent versions of RCRA requirements
Comprehensive reports of the various technologies	Examples include Refs. [276] and [278]
Reviews of competing technical approaches	
Pedagogical reviews on waste, waste characterization, and the various technologies	For instance, Ref. [369]
Classification of wastes and waste-form technologies	Examples include Refs. [277], [279], and [329]
Researchers and program managers	Within LMES and elsewhere

Table III. Four types of hazardous waste (after Refs. [363], [365], and [265])

Type of Waste	Traits	Comments
Declared	Classified as hazardous, based on knowledge	Irrespective of whether or not analysis reveals a hazard
Characteristic	Properties that would render a waste hazardous	Ignitable at low temperature ^a , corrosive ^b , reactive ^c , or toxic ^d
Listed	Known to be a threat to human health or the environment if improperly treated for disposal	Nonspecific source, specific source, acutely toxic, toxic, others listed by State agencies ^e
Mixture		

^aBelow 60° C.

^bAs examples, aqueous solutions with *pH* equal to or less than 2 or equal to or greater than 12.5 and liquids that corrode carbon steel at 55° C with a rate exceeding 6.35 mm y⁻¹.

^cMembers of this group are explosive or normally violently unstable without detonation, react violently with water, generate toxic gas when mixed with water, or defined by the Department of Transportation (DOT) as "forbidden", Class A, or Class B explosives.

^dSee Refs. [348g] and [363].

^eAs examples, polychlorobiphenyls (PCB's).

Table IV. Categories of waste, properties, and representative examples (after Refs. [277], [279], and [325])

Waste Category		General Properties	Representative Examples
1	Aqueous Liquids	Aqueous solutions with less than 1% organics Pumpable solids*	Acids (corrosive with $pH < 2$, sources include general waste water cleanup, plating lines, and electropolishing activities); bases (corrosive with $pH > 12.5$); reactive-cyanide (generally, with basic pH); toxic metal streams (e.g., Cd-, Cr-, Pb-, Hg-, and Se-containing streams); trace organics; Hg-containing solutions
2	Organic Liquids	Liquid streams with more than 1% organics	Nonhalogenated organic solvents (e.g., oils, methanol); halogenated organic solvents (e.g., F-, Cl-, Br-containing solvents, contaminated freon); scintillation cocktails in glass and plastic analysis bottles; Hg-containing organics
3	Inorganic Solids	Inorganic, non-metallic solids	Inorganic wet solids - sludges, filter cakes, and residues derived from waste-water cleanup and settling ponds; liquids sorbed onto solids such as vermiculite and clay; salt cakes (Cl- and NO ₃ -derived cakes with high water content) Inorganic dry solids - processing salts (mostly F-, Cl-, and NO ₃ -based); grouted and cemented sludges; ash, dusts, and fine particulates; contaminated soils derived from spills, leaks, cleanups, and waste burials); glass (process and laboratory equipment, window materials, vessels, bottles, light bulbs, glass beads, forms used within process equipment and for surface abrasion); ceramic crucibles, bricks, and media (oxide materials, beads, catalyst, reactor beds, milling and grinding media)
4	Metal Wastes	Inorganic, metallic solids	Ferrous metals; non-ferrous metals (e.g., Al, Cu, Cd); liquid mercury; lead shapes (bricks, casks, shielding); activated lead (reactor and accelerator, radiation field-derived Pb)
5	Organic Solids	Organic streams Candidates for direct incineration	Organic wet solids: absorbed combustibles (rags and paper used to wipe up spills); paint and residues; resins (spent organic resins, spent waste-water cleanup, C-filters); animal carcasses; sewage sludges Organic dry solids: wood (timbers with wood as the principal component); plastic and rubber (plastic sheeting, e.g., benelex and plexiglass, glovebox gloves not Pb-contaminated); paper, cloth, and rags (contaminated clothing and wipes); heavy sludges and asphalt (high-viscosity, unpourable sludges, radioactively contaminated asphalt, rock, and binders); graphite and carbon (crucibles and other components)

Waste Category	General Properties	Representative Examples
6 Heterogeneous Wastes	Solid materials that may contain a mixture ^b of organic, inorganic solid, and metallic materials	Construction, cleanup and process debris: commingled piping, wiring, wall materials, flooring, wood and plastic sheeting used for radioactive particulate containment, mixtures of combustible organic, metal, and ceramic materials
		Lab packs: mixtures of mostly solid chemicals in drums, vermiculite and other common packing material
		Equipment and gloveboxes: generally, metallic possibly containing oils, grease and process materials, electrical wiring and piping, packaged gloveboxes that may contain equipment, windows, gloves, and organic materials
		Filters: wood and metal frame HEPA filters, other metallic, organic, and ceramic process filters containing fine particulates
		Reactor equipment, experimental hardware, and fuel: listed chemicals, toxic metals that can become highly radioactive upon neutron irradiation
		Other toxic metal-containing materials: As-, Ba-, Cd-, Cr-, Se-, and Ag-contaminated
		Pb-containing components and materials: glovebox gloves, shielding aprons, and Pb oxide-containing rubber and plastic binder, Pb-acid batteries, Pb-wool, Pb-base solder materials
		Hg-contaminated materials: any general type, may be Ba-, Cd-, Cr-, Pb-, Se-, and Ag-containing
7 Special Solids	Streams that require special care or equipment ^c	Tritium wastes (liquid and solid); pyrophorics (reactive metals, e.g., Na and Na-metal alloys, particulate fines of Al, U, Be, Zr); nitrated rags and filters (stored, HNO ₃ -containing); compressed gasses (aerosol cans, gas cylinders); beryllium (Be) wastes (chips, dusts, other Be-contaminated materials); PCB-contamination

^a Solids content can be as high as 35 to 40 wt%.

^b Manufactured and packaging materials.

^c Including processes that are inconsistent with current radioactive materials handling guidance.

Table V. Classification of wastes, based on the impact of their chemical and physical properties on processing issues such as treatment, solidification, and disposal (after Ref. [331])

Waste Category	Waste No. From Table IV ^a	General Descriptions
Aqueous Liquids	Waste 1	See Table IV
Organic Liquids	Waste 2	See Table IV
Organic Sludges and Solids	Waste 4	See Table IV
Inorganic Sludges and Solids	Waste 3	See Table IV Includes cemented solids
Soils	None	Includes soils with less than 50% debris
Debris	Waste 6	See Table IV Organic Inorganic Heterogeneous
Lab Packs	None	With Metals without Metals
Reactive and Dangerous	None	Reactive Metals Explosives Compressed Gases
Inherently Hazardous	None	Liquid mercury (Hg) Elemental lead (Pb) Beryllium dust (Be) Batteries
Multiple	None	May require sorting
Other	None	Not fit other categories Not characterized

^aWaste Nos. are identified when the members of a category in this table are essentially identical to those in a category in Table IV.

Table VI. Stored mixed wastes within the DDT&E Program for which solidification technologies have not been specified, as of December 1993 (after Refs. [329], [331], [333], [335] and [336])

Waste Type (From Table V)	Specified Waste	Stored Waste-Volume		Total Volume	
		Absolute, m ³	Relative, Vol%	Absolute, m ³	Relative, Vol%
Aqueous Liquids ^a		261,297	44.9	261,297	44.9
Organic Liquids		16,622	2.9	16,622	2.9
Organic Sludges and Solids	Organic liquids (TRU)	1	0.0	4,252	0.7
	Organic sludges	3,875	0.7		
	Organic solids	376	0.1		
Inorganic Sludges and Solids	Calcine solids (dry)	3,600	0.6	193,705	33.3
	Cemented solids	169	0.0		
	Inorganic sludges	189,935	32.6		
	Inorganic solids (dry)	1	0.0		
Soils	Less than 50% debris	23	0.0	10,048	1.7
	Without debris ^b	10,025	1.7		
Debris	Inorganic ^c	28,418	4.9	75,299	12.9
	Heterogeneous	38,407	6.6		
	Organic ^d	8,474	1.5		
Lab Packs	With metals	169	0.0	268	0.0
	Without metals	99	0.0		
Reactive and Dangerous	Compressed gases	4	0.0	180	0.0
	Explosives	1	0.0		
	Reactive metals	175	0.0		
Inherently Hazardous	Batteries	17	0.0	1,090	0.2
	Beryllium dust (Be)	1	0.0		
	Elemental lead (Pb)	1,041	0.2		
	Liquid mercury (Hg)	31	0.0		
Multiple		16,314	2.8	16,314	2.8
Other		2,735	0.5	2,735	0.5
Total		581,810	100.0	581,810	100.0

^a Aqueous liquids contained in lab packs are included under the group, Lab Packs.

^b Includes cemented TRU solid waste.

^c Includes TRU.

^d Includes TRU.

Table VII. Various final waste forms and some of their advantages and disadvantages

Matrix Type	Material Base	Advantages	Disadvantages	Comments and Sources ^a
Inorganic	Portland Cement (PC) ^b	Wide variety of wastes	Increased volume	Extensive history
	PC-Clay	Low Weight	Bulking agent used ^{f,4}	Refs. [102], [151], [370], [383], [384], [391]
	PC-Flyash	Stability ^d	Incomplete chemical reactions	
	PC-Soluble Silicate ^e	Nontoxicity	Early processing removes water that must be replenished in later stages	Refs. [487], [488], [489], [490], [491], [492], [493]
	Gypsum ^h	Ambient-condition processing ^g		
	Kiln Dust ⁱ	Availability of raw materials		
	Lime-Clay Lime-Flyash	Mechanical properties		
Organic: Thermosets ^p	Reactive Flyash	No chemical additions		Experimental stage
	Sulfur-Polymer Cement	Mineral acid resistance	Low density ^l	Experimental stage
		High-saline resistance	Low melting point	Refs. [286], [287], [295], [299], [301], [303], [315], [316], [513], [519], [525]
		Waste-species immobilization ^j	Sensitive melt viscosity ^m	
		Impervious to water ^k	H ₂ S-Liberation ⁿ	
		Mechanical strength	Combustibility	
			Degradation ^o	
Organic: Thermoplastics	Epoxy-Based Polyethers	Multiple Waste Uses ^a	Permeability ^{v,w}	Unproven long-term stability
		Solvent-resistance	Instability ^x	Dearth of leaching data
		Water-resistance ^y	Reagent hazards	Proprietary technology
		Heat-resistance ^y	Syneresis	No commercial-scale field-test data
		Formulation ease ^z	Waste-induced degradation	Unknown microstructure ^{oo}
		Design versatility ^a	Incompatibility with aqueous residuals ^z	Refs. [187], [188], [197], [213], [220], [222], [240], [242], [366], [385]
Organic: Thermoplastics	Polybutadiene (Cross-linked)		Entrapment process	
	Polyethylene (Cross-linked)		Problematic wastes ^z	
	Polyurethane ^{ad}		Poor shelf life ^{aa}	
Organic: Thermoplastics	Unsaturated Polyesters		Standing water ^{ab}	
	Urea-Formaldehyde (UF) ^{ac}			
	Urea-Melamine ^{af}			
Organic: Thermoplastics	Bitumen ^{ag, ah}	Water-Based and Solvent-Based Wastes ^{ai}	Combustibility ^{am}	Unknown microstructure ^{oo}
		Waste-loading range ^{aj, ak}	Oxidant-induced fire risk	Emulsion-to-waste ratio must be in the range, 1:1 to 1:1.5 [366]
Organic: Thermoplastics		Flexible processing methods ^{al}	Osmotic swelling ^{an}	Refs. [8], [10], [182], [187], [188], [213], [220], [222], [253], [366], [377], [495], [510], [513], [514]
	Polyethylene			

Matrix Type	Material Base	Advantages	Disadvantages	Comments and Sources ^a
Vitrified	Silica-Based Glass	Potential for chemical stabilization of metals Chemically durable In-situ vitrification	Gas evolution Devitrification Low waste solubility Low density	Commercial for high-level waste [468] Commercial scale, including <i>in situ</i> vitrification [385] Refs. [103], [109], [118], [119], [120], [452], [477]
	Phosphate-Based Glass	Aqueous resistance ^{ap} Low-temperature processing	Pt-Lined melters ^{ay} Processing cycle ^{ax}	Ceramic waste Ceramic crucibles needed Ref. [454]
Devitrified	Glass-Ceramic	Ease of waste incorporation Wide composition ranges Leaching resistance Thermodynamic stability Mechanical durability	Chemistry needs tailoring Thermal cycles need to be established for optimum microstructure	Glass processing, followed by controlled devitrification Ref. [137], [138], [139], [140]
Ceramic	Rutile, t -TiO ₂	Chemical durability Low radionuclide loss	Mechanical properties	Encapsulation of high-level waste Refs. [414]
	Sodium Zirconium Phosphate ^{ax}	Wide waste compositions Low firing temperature	Radiolysis-derived H ₂ (g)-evolution	Potential additive to cement waste forms ^{ax} Ref. [415]
	Spinel ^{ax}	Very low aqueous solubility	Susceptible to acidic conditions Formation of Fe(OH) ₃	Nickel ferrite spinel (NiFe ₂ O ₄) is most studied spinel [412] Ref. [272]
	Synroc ^{ax}	Hydrothermal resistance Low leachability ^{ax}	Complicated process design	Extensively studied for high-level waste Solid solution ^{ax} Refs. [406], [411], [420], [426]
Metallic	Copper or Zinc Amalgams with Mercury Waste	Process flexibility	Very system-specific	Requires liquid mercury [364] Virtually no available literature
	Secondary Encapsulation (Vitromets and Cermets)	Thermal conductivity Mechanical strength Radiation protection	Incomplete wetting of primary glass or ceramic phase Incomplete encapsulation	Encapsulation glass or ceramic phases that contain waste Ref. [415]

^aThese references are typically general, broad-based, and nonspecific in scope and are cited to provide information on the character of the final waste form, its processing, and salient features. Reports of detailed studies are typically not included in this table because they appear elsewhere in this report.

^bCement is the major ingredient; minor additives may be present.

^cTypically, sodium silicate.

^dIncluding resistance to attack by water, UV-radiation, and biodegradation.

Matrix Type	Material Base	Advantages	Disadvantages	Comments and Sources ^a
				^a Temperature and pressure. ^f PC-clay, cement-flyash, lime-clay, and lime-flyash systems. [102] ^g Adds to the total solids (weight and volume), increases the waste viscosity, and prevents the settling of suspended components prior to solidification; these may be inert agents, such as Class F flyash, or reactive (pozzolan) agents, such as PC and lime. [102] ^h Calcium sulfate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, or its lower hydrates plus organic polymers or other organic additives; see text for details. ⁱ Cement and lime. ^j Problematic waste species, e.g., salts derived from boric acid, high saline concentrates, and sodium sulfate and similar salts. [525] ^k Sulfur is hydrophobic [317], if it is not oxidized [313]; metal sulfides formed during processing would likely behave similarly [313]. ^l Approximately 2000 kg m^{-3} [297], a relatively low value that can lead to segregation of higher-specific-gravity waste. [523,525] ^m For temperatures above the melting point [287], the level of impurities and other solutes [286,295,317], and the degree of S_8 -ring cleavage and chain formation [295,299,301] affect the viscosity. ⁿ At temperatures exceeding range over which melting occurs, i.e., above the range, 150 to 160° C. [525] ^o In some liquid media; examples include hot concentrated chromic acid, hot organic solvents, strong alkali, liquid containing strong oxidizing agents, aromatic and aliphatic hydrocarbons, and oxygenated liquids. [525] ^p Monomers in the liquid state are polymerized and cross-linked with the aid of catalysts [102,182,187,188,385]; polymerized material forms a spongy mass that entraps solid waste particles [366]; liquid associated with the waste remains after polymerization. [366] ^q Includes organic wastes (e.g., hydrocarbons, chlorinated hydrocarbons, pesticides), oil, and water-based wastes (i.e., when special emulsifying agents are used [80,84,102]). ^r Principally, owing to the hydrophobic nature of the monomer and prepolymer system. ^s That is, at moderate levels of heat. ^t Nearly an endless variety of compositions exists from which to select desired monomer compositions. ^u Mixing process may be either in-line or directly in the burial container. [385] ^v For polymer films, penetrant transmission rates are based on pressure, volume, and concentration measurements; see Ref. [226] for a summary of these methods and the salient transport phenomena that are likely to apply to waste forms considered herein. ^w The basic issues and principles that underpin the transport of small molecules (e.g., gases, vapors, and liquids) in polymers are known [198], although much appears to be needed to adapt these principles to polymeric final waste forms. ^x Toward UV-radiation and microorganisms. [187,221] ^y Derives from the resistance to wetting of the hydrophilic residuals by the hydrophobic polymer. ^z For urea-formaldehyde, sodium sulfate and related wastes and soap waste are difficult to entrap. [385] ^{aa} That is, for urea-formaldehyde resin emulsions. ^{ab} Water that remains on the surface of the drum or container being solidified. ^{ac} Essential details have not been studied. A working knowledge of the molecular and chemical structures and their physical characteristics [218] and the microscopic aspects of structure-related properties [219] seem generally unavailable, particularly for waste forms containing surrogate or real waste. ^{ad} Polyurethane contains the chemical group, $-\text{NHCOO}-$, formed via the reaction of a diisocyanate and a glycol [187] or other materials that terminate in hydroxyl groups, including polyethers, polyesters, and castor oil [214]. ^{ae} An aqueous emulsion of urea and formaldehyde, for which the polymerization is pH-dependent. [385] ^{af} Melamine is a triamine with the formula, $\{\text{C}(\text{NH}_2)=\text{N}\}_3$, where the symbols, { and }, designate a ring.

Matrix Type	Material Base	Advantages	Disadvantages	Comments and Sources ^a
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^a Includes bitumen which is a naturally occurring asphalt [8,10].

^a Composites with epoxy resins, urethane polymers, and various rubbers that are useful in tailoring the properties of bituminous coatings [200] are not included here.

^a Composites with epoxy resins, urethane polymers, and various rubbers that are useful in tailoring the properties of bituminous coatings [200] are not included here.

^a Range is wide, particularly for reactor waste streams. [385]

^a Ratio of matrix to waste is generally high, being on the order of 1:1 to 1:2 based on dry weight. [366]

^a Examples include evaporation methods, emulsification techniques, and extrusion.

^a Much is known about the flammability of these and related polymers, and the flammability retardation is an active research area for these materials. [199]

^a Induced by soluble salts.

^a Essential details have not been studied. As examples, the molecular and chemical structures and their physical characteristics [218] and the microscopic aspects of structure-related properties [219] seem to be not very well characterized.

^a Below 100° C.

^a Potentially complicated.

^a Sodium phosphate glass.

^a Including synthetic monazite, a mixed lanthanide orthophosphate, LnPO_4 , where Ln = La, Ce, Nd (as examples).

^a Increases retention of Cs, Ba, and Sr.

^a General formula, AB_2O_4 , e.g., MgAl_2O_4 , $(\text{Fe,Ni,Mn})\text{Al}_2\text{O}_4$, and NiFe_2O_4 . [54,60]

^a The principal phases of interest are perovskite (CaTiO_3), zirconolite ($\text{CaZrTi}_2\text{O}_7$), and hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$). [410]

^a About 0.001 of those for borosilicate glass (95° C).

^a Ti-, Zr-oxide rich matrix.

Table VIII. Summary of inorganic systems

System	Raw Materials or Starting Components	Basic Chemistry and Physics of Process	Common Variants	References
Portland Cement (PC)	Lime, CaO (C) ^a Iron Oxide, Fe_2O_3 (F) ^b Silica, SiO_2 (S) ^c Alumina, Al_2O_3 (A) ^d Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ^e Magnesia, MgO ^f	(1) CaO , SiO_2 is heated ($\sim 1480^\circ\text{C}$); after $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is added, the mixture is finely ground (2) Ca-silicate mixture, predominately comprised of C_3S and C_2S , and small amounts of C_3A and C_4AF ^{g,h} (3) Water ⁱ reacts with PC, forming hydrated silicates and aluminates	(1) High- Al_2O_3 cement ^{j,k} (2) Additives to control the setting and curing rates (3) Dispersants to retard the formation of cementitious gels ^l (4) Acids and bases to alter setting	[24], [27], [29], [30], [45], [151], [383], [390], [392], [393]
Gypsum-Based Matrix	Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Similar to that described for PC ^m	Various solids additives ⁿ	[385], [390], [487], [488], [489], [490], [491], [492], [493]
Sulfur-Polymer Cement (SPC)	Sulfur, S_8 ^o Cyclopentadiene, C_5H_6 Dicyclopentadiene, $\text{C}_{10}\text{H}_{12}$	(1) Solid S_8 is melted ^p (2) Chemical modifiers that improve melt plasticity are added (3) Time-temperature cycles are regulated to attain desired polymerization ^q (4) Melt is cooled or quenched to solidify	(1) Solid aggregate ^r is added to the melt ^s (2) Glycol used as a chemical modifier	[304], [305], [314], [316], [525]

^aSources: Alkali waste, calcite, cement rock (i.e., an argillaceous limestone [23,29]), chalk (i.e., a soft limestone of organic origin, being essentially composed of the calcareous remains of marine organisms [23]), Fuller's earth (i.e., a natural, fine-grained earthy material, such as clay, with a high adsorptive power, consisting mainly of hydrated aluminum silicates [349]), limestone, marble, marl (i.e., mineral composed of a mixture of chalk and clay [23]), seashells, shale, slag. [383]

^bSources: Blast furnace flue dust, clay, iron ore, mill scale, ore washings, pyrite cinders, shale. [383]

^cSources: Calcium silicate, cement rock, clay, flyash, Fuller's earth, limestone, loess, marl, ore washings, quartzite, rice hull ash, sand, sandstone, shale, slag, traprock. [383]

^dSources: Aluminum ore refuse, bauxite, cement rock, clay, copper slag, flyash, Fuller's earth, granodiorite, limestone, loess, ore washings, shale, slag, staurolite. [383]

^eSources: Anhydrite, calcium sulfate, gypsum. [383]

^fSources: Cement rock, limestone. [383]

^gNomenclature gives the relative number of moles within the various phases; see text and previous column for the meanings of C, S, A, and F.

^hRelative amounts of components in a typical ordinary cement: 50 wt% C_3S , 25 wt% C_2S , 10 wt% C_3A , 10 wt% C_4AF , and 5 wt% other oxides. [151,383]

ⁱMinimum amount of water needed for "workability" (i.e., the consistency of the cement mix that permits it to be transported, placed, and finished with sufficient ease but without segregation of the components [29]) is approximately 28.6 wt% for Portland cement; the exact amount varies with the presence of solids (e.g., solid waste) that tend to absorb large amounts of water. [30,383]

^j Mainly consists of $\text{CaO} \cdot \text{Al}_2\text{O}_3$ (CA).

^k Strength may decline with time in high-temperature environments and when the cement mix has a high water content. [29,30,383]

^l As examples, sulfonate and carboxylate compounds.

^m See text for discussion on the paucity of data regarding gypsum systems that seems to characterize the technical literature.

ⁿ Examples include sand, expanded perlite, and exfoliated vermiculite aggregates. [142,143,144,145]

^o Principally consists of mixtures of the S_6 , S_8 , and S_{12} crystallographic forms [287,295,297,303]; see text for details.

^p Depending on the composition of the allotropic mixture, the temperature range over which melting can occur is 106 to 119° C.

^q Changes that occur in the melt during processing involve the number of S-atoms per ring, the degree of polymerization, the molecular weight distributions, the relative concentrations of ring and chain molecules. [286,295,297,298,303]

^r Other particulate materials, such as mica and quartz, may be used.

^s This variant leads to sulfur concrete.

Table IX. Summary of organic thermosetting systems

System	Raw Materials or Starting Components	Basic Chemistry and Physics of Process	Common Variants	References
Urea-Formaldehyde (<i>UF</i>)	Urea, $H_2NC(O)NH_2$, Formaldehyde, $HC(O)H$	(1) Hydroxymethylation of urea and low molecular weight urea-formaldehyde derivatives is carried out (2) Condensation is carried out to obtain the desired degree of polymerization (3) Aqueous resinous solution is either heated, under reduced pressure, to reduce the water content or spray dried to yield a resin powder (4) Component is formed (e.g., in a mold) (5) Resins are cured to obtain complete polymerization and network microstructure	Polyurethane	[187], [196], [231]
Epoxy-Based Polyethers	Bisphenol A, $HO-\phi-C(CH_3)_2-\phi-OH$ Epichlorohydrin, Compound (XVI) ^a Co-reactant ^b	Similar to that for <i>UF</i>		[204], [208], [240], [242]
Unsaturated Polyesters	Diol, $HO-R-OH$ Dicarboxylic acid, $HO-C(O)-R'-C(O)OH$ Styrene, $CH_2=C(\phi)H$	(1) Condensation of diol and dicarboxylic acid is carried out, with the generation of by-product water (2) Component is formed (e.g., in a mold) (3) Polymer chains are cross-linked, via addition polymerization	Hydroxycarboxylic acid, $HO-R-C(O)OH$ Organic acid chloride Cross-linked poly(vinyl esters)	[187], [188]

^aSee p. 45.

^bExamples include polyamines, polyamides, polyphenols, polycarboxylic acids, and anhydrides. [204, 208, 240, 242]

Table X. Summary of organic thermoplastic systems

System	Raw Materials or Starting Components	Basic Chemistry and Physics of Process	Common Variants	References
Bitumen	Petroleum crude	(1) Distillation of the crude to remove volatile components (2) Solvent extraction ^a to remove gas oils and similarly soluble components	Air-blown (oxidized) bitumen Emulsified bitumen Distillation-controlled composition	[8], [9], [10], [376], [378]
Vinyl-Based Polymers	Ethylene, $\text{CH}_2=\text{CH}_2$ Initiator Catalyst	Bulk or solution polymerization	Other vinyl compounds, $\text{CH}_2=\text{C}(\text{X})\text{H}^b$ Solution Polymerization Suspension Polymerization Emulsion Polymerization	[371], [510], [513], [514]
	Propylene, $\text{CH}_2=\text{C}(\text{CH}_3)\text{H}$ Initiator Catalyst		Other vinyl compounds, $\text{C}(\text{CH}_3)\text{H}=\text{C}(\text{X})\text{H}^c$ Solution Polymerization Suspension Polymerization Emulsion Polymerization	

^aUsing hexane, for example.

^bStyrene (X = phenyl, C_6H_5 -), vinyl chloride (X = Cl), vinyl acetate [X = $\text{CH}_3\text{C}(\text{O})\text{O}$], acrylic acid [X = $\text{C}(\text{O})\text{OH}$], and acrylamide [X = $\text{C}(\text{O})\text{NH}_2$] groups are common examples.

^cEspecially, methyl methacrylate [X = $\text{CH}_3\text{C}(\text{O})\text{O}$].

Table XI. Summary of vitrified systems

System	Raw Materials or Starting Components	Basic Chemistry and Physics of Process	Common Variants	References
Silica-Based Glasses	Silica, SiO_2 Alkali metal oxides Alkaline earth metal oxides Boron oxide, B_2O_3	(1) Oxides are melted, along with salts that help to control the melt properties (2) Bubbles are removed in a fining stage (3) Composition and thermal variations are removed via homogenizing steps (4) Specimens are formed via various processes (e.g., casting, drawing, blowing, extrusion)	Oxyhalide glasses Oxynitride glasses Oxycarbide glasses Addition of polyatomic anions*	[54], [73], [109], [124], [180]
Phosphate-Based Glasses	Phosphorous pentoxide, P_2O_5 Alumina, Al_2O_3	(5) Melt is cooled under controlled conditions to yield glass with the desired properties		

* Examples include carbonate, nitrate, nitrite, sulfate, dichromate, and selenate glasses. [124]

Table XII. Summary of devitrified (glass-ceramic) systems

System	Raw Materials or Starting Components	Basic Chemistry and Physics of Process	Common Variants	References
Silicate-Based Glass-Ceramics	Silica, SiO_2 Alkali metal oxides Alkaline earth metal oxides Boron oxide, B_2O_3	(1) Make initial glass, according to Table XI and related text* (2) Thermally treat to nucleate amorphous (preceramic) oxide phases	Spinodal decomposition of glassy phases to yield interconnected phases Sol-Gel processing	[54], [65], [73], [137], [138], [140]
Aluminosilicate-Based Glass-Ceramics	Silica, SiO_2 Alkali metal oxides Alkaline earth metal oxides Boron oxide, B_2O_3 Alumina, Al_2O_3	(3) Thermally treat to crystallize ceramic phases from amorphous phases yield glass with the desired properties		

* See the section, Vitrified Matrices (p. 64).

Table XIII. Summary of ceramic systems

System	Raw Materials or Starting Components	Basic Chemistry and Physics of Process	Common Variants	References
Single-Component Ceramics ^a	Ceramic Powder(s) Dispersant ^b Sintering aid ^c	(1) Ball mill to reduce the particulate size and to mix the powders (2) Disperse particulates in aqueous media, under suitable conditions (e.g., <i>pH</i> and dispersants) (3) Cast to concentrate the particulates (4) Dry the cast specimen (5) Calcine amorphous phases crystalline, if needed (6) Decompose and burn off organic dispersants (7) Sinter	Pressing Plastic-Forming Sol-Gel Polymerization Spray-Drying	[48], [55], [64], [65]
Multicomponent Ceramics ^d				

^aOxide examples include alumina (Al_2O_3) and rutile ($t\text{-TiO}_2$).

^bOrganic polymers, e.g., derivatives of poly(methacrylic acid), organic surfactants, such as fatty acids, and inorganic compounds (e.g., sodium silicate) are common examples. The members of each dispersant group alter the surface properties of the particulates, albeit via different mechanisms.

^cCeramic materials, such as MgO , when it is used as a dopant, as for the densification of alumina, and Y_2O_3 and SiO_2 , either of which aids the densification process by liquefying at high temperature and, thereby, providing a medium for the migration of chemical species.

^dOxygen-based examples include mullite, whose composition is $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, spinel, which has the general formula, AB_2O_4 , e.g., MgAl_2O_4 , $(\text{Fe}, \text{Ni}, \text{Mn})\text{Al}_2\text{O}_4$, and NiFe_2O_4 , and Synroc, whose principal phases of interest are perovskite (CaTiO_3), zirconolite ($\text{CaZrTi}_2\text{O}_7$), and hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$) [100,410]. See text for details.

Table XIV. Properties characterizing final waste forms (after Refs. [171] and [279])

Property ^a	Typical Desired Values	Derivation	Comments
<i>High Priority</i>			
RCRA Solid	No free water	Standard test (paint filter test) [363,365]	Regulated by EPA [268,360,361,362,363,364]
RCRA Toxicity	Pass Toxicity Characteristic Leach Procedure (TCLP)	Concentration-based standard	Regulated [360,362,363,364,370] Limits set by Best Demonstrated Available Technology (BDAT) [354,363]
Free-Standing Liquid	Radioactive waste: Less than 0.5 vol% free drainable liquid Nonradioactive waste: Less than 0.5 vol% free drainable liquid	Radioactive waste: ANSI/ANS-55.1 test Nonradioactive waste: Evaluation of standing water and syneresis	Radioactive waste: Regulated by NRC Nonradioactive waste: Standard test is not available; modified ASTM tests permitted
Stabilization	Chemical fixation	EPA guidance	Related to flexibility constraint in Table I; refer to Table IV Highly desirable; preferred to physical encapsulation Standard test is not available; may be indirectly measured by the TCLP
Utilization Experience	Technical demonstration exists	Includes field (commercial) scale, pilot scale, laboratory scale, principle	Desirability: field (commercial) scale > pilot scale > laboratory scale > principle
Reactivity (WF)	Not reactive	Characteristic test [363,365]	See Table III
Toxicity (WF)	Not toxic	Characteristic test [348g,363]	See Table III
Flammability (WF)	Not ignitable below 60° C	Characteristic test [363,365]	See Table III
Corrosivity (WF)	Not corrosive [363,365]	Aqueous solution pH : $2 < pH < 12.5$ Other liquids: Not corrode carbon steel at 55° C faster than 6.35 mm y ⁻¹	See Table III
<i>Medium Priority</i>			
Gas Generation (WF)	None or controlled release during storage and burial	From radiolysis and not volatilization of liquids such as water	Design process to deal with gases
Melting Point	Must exceed 50° C	Maintain physical dimensions and remain in solid form at elevated temperature in storage and landfill	The term, melting point, may be too imprecise; includes softening
Waste-Stream Compatibility	Can successfully solidify and stabilize a variety of wastes	Includes oxidants, organic solvents, highly soluble salts, insoluble compounds, sludges with oxides	Insensitivity to waste composition is desirable; K- and Na-salts are examples of highly soluble salts

Property ^a	Typical Desired Values	Derivation	Comments
Gas Generation (Process)	None or controlled acidic (e.g., HCl and SO ₂) or toxic (e.g., CO and H ₂ S) off-gases	EPA standards [338,342]	Other problematic gases may contain Hg, Tc, Cs, I, Cd, As, or various organic species Design process to deal with gases
By-Products	Not hazardous	Secondary waste	Includes HEPA filters, wash water, scrubber solutions, and off-gases
Flammability (Process)	Complies with safety standards	OSHA standards [339]	Design process to deal with flammable materials
Reactivity (Process)	Not reactive	Characteristic test [363,365]	Reactive characteristic not permitted; see Table III
Set Time (WF)	Short, as allowed by permits	Duration required for solidification to occur	Establishes the limits for handling and shipping the final waste form
Toxicity (Process)	Not toxic	Characteristic test [348g,363]	Toxic characteristic not permitted; see Table III
Volume Increase, %	A decrease or minimal increase	Change in bulk specific volume of waste-matrix system, expressed as a percentage of the bulk specific volume of the original waste	Storage and burial costs directly relate to bulk volume
Physical Stability Toward Immersion In Water	Monolith: Fraction of compressive strength retained after 90 days Other:	Monolith: Retention of critical fraction of original strength Other: Size-dependent stability	Non-monolithic WF may possess, as examples, granular or foam-like configurations
Leach Resistance	Leachability index of 6 or greater	Standard test [368] Monolith: Semidynamic leach conditions, comprising multiple stages	Includes formulations Leach index taken as the negative logarithm of the diffusion coefficient
Particle Size (Process)	Complies with safety standards	OSHA standards [339]	Design process to deal with finely divided solids
Waste Loading	Maximum loading	Levels are high, medium, and low	Desirability: high > medium > low
Corrosivity (Process)	Intermediate stages do not produce by-product streams that are corrosive by characteristic test	Aqueous solution pH: $2 < pH < 12.5$ Other liquids: Not corrode carbon steel at 55° C faster than 6.35 mm y ⁻¹	Corrosive characteristic is undesirable
Temperature	Less than 1800-2000° C	Materials processing limitations	Special equipment needed for higher temperatures
Aging/Time Dependence	Insignificant degradation of properties	Adequate kinetic or thermodynamic stability or metastability	Long-term performance for monolithic waste form
Durability After Thermal Cycling	Fraction of compressive strength retained after 30 cycles	Compressive strength under a 345-kPa (50-psi) load after thermal cycling with that before thermal cycling	Physical integrity must be retained
Process Recovery	Short startup time after an interrupting shutdown	Process design standards	Equipment and lines may need to be cleaned prior to startup
Unconfined Compressive Strength	Minimum value is 414 kPa (60 psi)	Standard test	NRC and RCRA requirement
Homogeneity	Representative sampling is possible	Macroscopic and microscopic profiles	Regarding waste and binder

Property*	Typical Desired Values	Derivation	Comments
Radiation Stability	Fraction of compressive strength retained	Exposure to 10^5 rads	No requirements under <i>RCRA</i>
<i>Low Priority</i>			
Biodegradation	No Growth	Adequate resistance against microbial attack	NRC requirement may warrant medium-high priority; no requirements under <i>RCRA</i>
Particle Size (WF)	Minimum particle size of free, air-borne particulates is 1-5 mm	Free, air-borne acicular particles are not allowed	Prevention of undesirable respirable particles during storage may warrant higher priority
Void Fraction	No open porosity	Void fraction should not contain waste-derived gases	Germane to structural stability of low-level waste
Criticality	Below critical conditions	No sustained nuclear chain-reaction	Germane to radioactive properties and critical mass of active (fissile) isotopes Not pertinent for hazardous waste; probably not an issue for low-level and mixed waste

*Parenthetical terms, WF and Process, refer to the waste form and the overall process by which waste is incorporated into the waste form, respectively.

Table XV. Sample form for assessing competing waste-form technologies for suitability with a single type of waste, based on Table XIV

Performance Criterion ^a	Generic Waste-Form Technologies and Representative Materials ^b								
	Inorganic		Organic				Vitrified	Devitrified	Ceramic
	<u>Cement</u>	<u>Sulfur-Polymer</u>	<u>Thermosets</u>		<u>Thermoplastics</u>		<u>Glass</u>	<u>Glass-Ceramics</u>	<u>Mullite</u>
	(Grout)	Cement	(UF ^c Resin)	(Epoxy-Based)	(Bitumen)	(PE)	(SiO ₂ -Based)	(Al ₂ O ₃ , SiO ₂ -Based)	(3Al ₂ O ₃ ·2SiO ₂)
<i>High Priority</i>									
RCRA Solid									
RCRA Toxicity									
Free-Standing Liquid									
Stabilization									
Utilization Experience									
Reactivity (WF)									
Toxicity (WF)									
<i>Medium Priority</i>									
Gas Generation (WF)									
Melting Point									
Waste-Stream									
Compatibility									
Flammability (WF)									
Gas Generation (Process)									
By-Products									
Flammability (Process)									
Reactivity (Process)									
Set Time (WF)									
Toxicity (Process)									
Volume Increase, %									
Physical Stability Toward									
Immersion In Water									
Leach Resistance									
Particle Size (Process)									
Waste Loading									
Corrosivity (Process)									

Temperature									
Aging/Time Dependence									
Durability After Thermal Cycling									
Corrosivity (WF)									
Process Recovery									
Unconfined Compressive Strength									
Homogeneity									
Radiation Stability									

Low Priority

Biodegradation									
Particle Size (WF)									
Void Fraction									
Criticality									

* Criteria pertain to the waste forms; however, the parenthetical terms, WF and Process, are used to distinguish the assessments of the waste form and other important aspects of the process, respectively, when the property must be assessed for both.

^b The parenthetical materials are included as examples; their inclusion in this table is not an endorsement of their use.

^c VES is another common thermosetting material.

Table XVI. Summary of candidate alternative waste-form technologies, their primary representative, and their main features

Waste-Form Family	Representative	Main Features	Immobilization Mechanism
Inorganic	Sulfur-Polymer Cement	Polymeric chains of rings Some cross-linking Polycrystalline solid Thermoplastic melt	Encapsulation
Organic Thermosetting	Cross-linked <i>UF</i> Resin or <i>VES</i> Resin	Cross-linked polymeric chains Rigid Little interaction with waste species	Encapsulation
Organic Thermoplastic	Bitumen	Colloidal dispersion; continuous liquid phase Fluidity; requires secondary containment Little interaction with waste species	Encapsulation
	Polyethylene	Essentially linear, interpenetrating chains Some crystallinity Little interaction with waste species	Encapsulation
Devitrified	Glass-Ceramic, based on Al_2O_3 and SiO_2	Predominantly crystalline Glassy intergranular phase Complex chemistry Good metastability	Encapsulation Potential for chemical fixation in two phases Potential for secondary encapsulation
Ceramic	Any based on Al_2O_3 and SiO_2	Polycrystalline Complex chemistry	Encapsulation Potential for chemical fixation
Metallic	Amalgam	Treatment for liquid mercury	Encapsulation

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