Preliminary Evaluation of the Characteristics of Nuclear Wastes Relevant to Geologic Isolation in Basalt

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MASTER

May 1978

Prepared for the United States
Department of Energy
Under Contract EY-77-C-06-1030

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PRELIMINARY EVALUATION OF THE
CHARACTERISTICS OF NUCLEAR WASTES
RELEVANT TO GEOLOGIC ISOLATION IN BASALT

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A B S T R A C T

The physical and chemical characteristics of radioactive waste which have bearing upon the concept of geologic storage in basalt are reviewed and discussed. Each class of waste form (spent unprocessed fuel, calcine, glass, and supercalcine) has its own unique characteristics which may or may not affect the concept of final storage of radioactive waste in basalt. These characteristics form the basis for scientific evaluation of the relative merits of each of the waste/basalt pairs.

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INTRODUCTION

NUCLEAR WASTE FORMS

The present emphasis in the United States' Terminal Storage Program is not to reprocess spent fuel elements. Due to this directive, we are considering spent unprocessed fuel to be our prime radioactive waste form to be stored in a potential basalt cavern.

If the decision were made to reprocess spent fuel with its resultant high-level waste stream, a vitrification process yielding a glass product would probably be the leading contender for the solid waste form, since it has, to date, received the majority of research and development funding. However, calcine has not been ruled out by many investigators and a number of "advanced alternatives" to glass have received some attention.

In order to insure the comprehensiveness of our current waste/basalt interaction studies, we have chosen to include the following waste forms in our experiments: spent unprocessed fuel; calcine; glass; and, supercalcine. The emphasis in our program during fiscal year 1977 was on glass, since, at that time, it was the leading high-level waste form candidate.

As a first step in analyzing the physical and chemical effects of storing nuclear waste in an underground basalt repository, one must first deal with the waste forms themselves. Needless to say, each waste form has its own set of unique characteristics (chemical and radiological composition, mineralogy, structure, thermal energy, etc.) which will have a direct bearing upon the storage concept.

Fortunately, much of this information is already available in the literature. Battelle-Northwest recently compiled data through 1975 on all aspects of the back-end of the nuclear fuel cycle.¹ A recent publication² updates some of the concepts concerning advanced waste forms and also includes an in-depth discussion of the factors governing waste/basalt interaction. Rather than duplicate these efforts once again, we are viewing these reports as a foundation for the discussion which follows. To help achieve this end, we are also including, as Table I, a summary table adapted from a recent U. S. Nuclear Regulatory Commission Report.³ Spent unprocessed fuel has been added to the table in an effort to be comprehensive. Since data on spent unprocessed fuel are sparse, approximate values were sometimes assigned using the assumption that spent unprocessed fuel is composed of nearly 96-97 weight percent of the various isotopes of uranium and, since data on uranium oxide are commonly available, these data would reflect actual spent unprocessed fuel characteristics. When these approximations were made, they were so noted on Table I.

The purpose of the present document is to review waste form characteristics and to discuss the relevancy of these characteristics upon the concept of storage of nuclear waste in basalt.

THERMODYNAMIC STABILITY AND STRUCTURAL STATE

The structural state of the components of a waste form is an important and not widely appreciated parameter governing its reactivity. Consider the case of a

TABLE I
PROPERTIES OF RADIOACTIVE WASTE FORMS (ADAPTED FROM NUREG-0279)

PROPERTY	UNITS	SPENT FUEL PELLETS	SALT CAKE	SPRAY CALCINE	POT CALCINE	ROTARY KILN CALCINE	FLUIDIZED BED CALCINE	SUPER CALCINE POWDER	SUPER CALCINE CERAMIC	COATED PARTICLES	PHOSPHATE GLASS	BORO- SILICATE GLASS	SINTERED PROCESS	GLASS CERAMIC	NEPHELINE SYENITE	METAL MATRIX	ION EXCHANGE	ROCK MELT
SOLUTION RATE	$\frac{\text{mg}}{\text{m}^2 \text{ sec}}$	10^{-2} to 10^{-5}	10^3 to 10^6	10 to 100	10 to 100	10 to 100	10 to 100	10^{-6} to 10^{-4}	10^{-7} to 10^{-5}	10^{-6} to 0.01	10^{-5} to 0.7	10^{-5} to 0.01	10^{-5} to 0.01	10^{-5} to 10^{-3}	10^{-5} to 0.7	10^{-5} to 10^{-2}	0.001 to 0.01	10^{-5} to 0.01
CORROSION TO CLAD MATERIAL	nm/sec	*	0 to 10^4	0 to 10	0 to 10	0 to 10	0 to 10	0 to 10	0 to 10	0 to 10	0 to 10	0 to 10	0 to 10	0 to 10	0 to 10	0 to 10	0 to 10	NA
RESIDUAL NITRATE AND/OR WATER	%	<.005	0.20 to 30	<4.0	<0.05	<4.0	<.03	0.005 to 0.05	0.005 to 0.01	0.005 to 0.05	0.005 to 0.05	0.005 to 0.05	0.005 to 0.05	0.005 to 0.05	0.005 to 0.05	0.005 to 0.05	0.005 to 0.05	<10.0
MAXIMUM PROCESSING TEMPERATURE	°K	NA	310 to 720	970	695	870 to 1,070	670 to 1,070	1,370 to 1,570	1,370 to 1,570	1,670	1,170	1,270 to 1,670	1,235 to 1,370	1,270	1,620	1,470	1,670	1,000
RUTHENIUM VOLATILIZED AT PROCESSING	%	NA	<1.0	<1.0	5 to 30	<1.0	Insignificant	<7.0	<5.0	<10.0	3 to 15	<2.0	<10.0	<10.0	<10.0	<10.0	<10.0	<5.0
VOLATILITY	NA	NA	1,000°K all Ru & Cs	1,200°K all Ru & Cs	1,200°K all Ru & Cs	1,200°K all Ru & Cs	1,200°K all Ru & Cs	1,570°K some Ru & Cs	1,670°K much Ru & Cs	1,670°K all Ru & Cs	<1,500°K all Ru & Cs	<1,500°K all Ru & Cs	<1,370°K all Ru & Cs	<1,325°K all Ru & Cs	<1,620°K all Ru & Cs	<1,525°K all Ru & Cs	<1,670°K all Ru & Cs	NA
SPECIFIC VOLUME	$\frac{\text{m}^3}{\text{MgU}}$	—	0.05 to 1.0	.03 to .06	0.044 to 0.058	0.045	0.032 to 0.040	0.010	0.010	0.130	0.036 to 0.078	0.04 to 0.1	0.03 to 0.055	0.077	0.08	0.08	0.050	4 to 40
WEIGHT PERCENT WASTE PRODUCT OXIDES	MAXIMUM TYPICAL	5% 4%	<80% <80%	<100% <100%	<90% <90%	<100% <100%	<100% <100%	<75% 45%	<75% 45%	<80% 45%	<25% 20%	<50% 20-35%	<50% 45%	30% 25%	50% 20%	<65% 33%	<80% 25%	10% 5%
SPECIFIC AREA	$\frac{\text{m}^2}{\text{Kg}}$	—	100 to 5,000	10,000 to 20,000	100 to 5,000	100 to 5,000	100 to 5,000	10,000 to 20,000	0.005 to 0.05	100 to 5,000	0.005 to 0.05	0.005 to 0.05	0.1 to 1.0	0.005 to 0.05	0.005 to 0.05	0.005 to 0.05	0.005 to 0.05	NA
FORM	NA	Fractured Pellets	Mono- lithic	Powder	Powder or Scale	Powder	Granular	Powder	Monolithic	Beads	Fractured Monolith	Fractured Monolith	Pellets	Mono- lithic	Mono- lithic	Mono- lithic	Mono- lithic	In Situ Melt
STRUCTURAL QUALITY	NA	Very Hard & Brittle	Crumbly	Soft & Crumbly	Soft & Crumbly	Soft & Crumbly	Soft & Crumbly	Soft & Crumbly	Very Hard & Brittle	Hard	Very Hard & Brittle	Very Hard & Brittle	Very Hard	Hard & Tough	Very Hard & Brittle	Hard & Ductile	Hard & Brittle	Hard
POROSITY	%	2 to 10	0	30 to 75	40 to 85	70 to 80	45 to 80	40 to 80	2 to 20	<20.0	<5.0	<1.0	8 to 25	<10.0	<5.0	<10.0	<3.0	<5.0
DENSITY	$\frac{\text{Kg}}{\text{m}^3}$	10,000 to 10,500**	1,700	1,000 to 2,400	1,100 to 1,400	1,000 to 1,300	2,000 to 2,400	4,000	3,500 to 4,000	1,700	2,700 to 3,000	3,000 to 3,600	2,400 to 3,300	2,850	3,000	2,400 to 5,500	<4,500	2,700
COEFFICIENT OF LINEAR EXPANSION	$\times 10^{-6}/^\circ\text{K}$	~10**	0	~8.3	~8.3	~8.3	~8.3	~8.3	8 to 10	~4.5	8 to 10	8 to 10	~8.0	9.0 to 1.3	~10	~29	~4.2	9.0 to 4.0
THERMAL CONDUCTIVITY	$\frac{\text{W}}{\text{m}^\circ\text{K}}$	2** to 6	0.1 to 0.5	0.2	0.35 to 1.0	0.2	0.2 to 0.3	0.6	0.8 to 2	17	0.8 to 1.3	0.9 to 1.3	0.7	2.2	1.2	5 to 35	1.2	1.0 to 1.5
HEAT CAPACITY	$\frac{\text{J}}{\text{Kg}^\circ\text{K}}$	238** to 330	500 to 800	650	650	650	650	670	1,100 to 1,200	680	1,100 to 1,200	750	1,100 to 1,200	1,100 to 1,200	1,100 to 1,200	350	550	1,000 to 1,600
LIQUIDUS TEMPERATURE	°K	<3,138**	520	1,670	1,670	1,670	1,670	1,670 to 1,870	1,670 to 1,870	2,570	820 to 1,020	800 to 1,500	970 to 1,500	1,070	850	600	2,290	1,320
TRANSITION TEMPERATURE	°K	NA	NA	NA	NA	NA	NA	NA	NA	NA	770	870 to 970	NA	NA	900	***	NA	NA

KEY TO SYMBOLS

— = Not Available.

NA = Not Applicable.

* = Mostly stress corrosion cracking which is localized, variable, and dependent upon the chemical species.

** = Based on UO₂ with approximately 2-10 percent porosity.

*** = Alloy has a transition temperature.

Particular chemical composition that, by variations in processing, can be either rapidly dried from a liquid to give a non-crystalline powder (= calcine), or melted into a glass, or slowly cooled to give the stable crystalline form for that composition. The free energy states of the three solids can be represented schematically as in Figure 1 (A).

A fundamental law of chemical reactions states that a reaction proceeds in the direction of lower free energy (G). Figure 1 (A) is a schematic presentation of the fact that, for a given chemical composition, the calcine and glass forms are unstable with respect to the stable crystalline phase form at the temperature of interest. The calcine and glass have excess free energy compared to the crystalline form due to their more disordered structural states. This is the reason that devitrification (crystallization) studies are such an important part of glass waste form evaluation. It is not enough to evaluate the properties of the metastable glass alone when the possibility exists that the glass will devitrify at some time during its functional lifetime.

Our studies are not aimed at phase changes in a solid, from less to more stable forms, but in reactivity in a geologic environment. The disordered structural state which results in excess free energy for calcine and glass can also enhance reactivity. Thermodynamics predict when a reaction can occur, but does not predict that it will occur. There is often a substantial activation energy blocking a thermodynamically favorable reaction. Consider again, the three solid forms of the same composition. In Figure 1 (B), it is seen that the crystal can undergo some reaction, for example dissolution

(A)

(C)

(B)

FIGURE 1

- (A) SCHEMATIC REPRESENTATION FOR THE RELATIVE FREE ENERGIES OF THREE SOLID FORMS OF THE SAME CHEMICAL COMPOSITION.
- (B) SCHEMATIC REPRESENTATION OF THE ACTIVATION ENERGY BARRIER FOR A THERMODYNAMICALLY FAVORABLE REACTION FOR EACH OF THE THREE SOLID FORMS.
- (C) PHASE DIAGRAM FOR THE SYSTEM A-H₂O WHERE A HAS TWO POLYMORPHIC FORMS α AND β . BELOW T_{tr} , β IS MORE SOLUBLE THAN α .

in water, but a substantial activation energy first needs to be overcome. That activation energy is less for the calcine and glass because of their excess free energy. A clear illustration of this is provided by the work of Hawkins and Roy⁴ on the hydrothermal alterations of basalts. They compared the reactivity of the crystalline basalts with chemically identical glasses and desiccated gels ($\approx$ calcine) and found that "for a given crystalline rock, glass and gel, all of the same composition (with other conditions constant...), the glass and gel were readily altered while the crystalline rock was altered only slightly, if at all."

Indeed, desiccated gels and glasses as starting materials have been used for the last three decades of hydrothermal mineralogy and petrology studies because they are so reactive and, therefore, provide a more rapid approach to equilibrium.⁵

Another example of why the thermodynamic state of a solid is relevant to waste reactions is illustrated in Figure 1 (C). Phase A has two crystalline forms α and β . At all temperatures below T_{tr} , the phase β is metastable and has excess free energy. It is more soluble in water.

Based on the above discussion, it is to be expected that calcine and glass waste forms will be more reactive in the geologic environment than the largely crystalline forms spent unprocessed fuel and supercalcine.

Because of the importance of this concept to waste/basalt interactions, the thermodynamic state of the phases (crystalline or noncrystalline) is a major waste form

characteristic and will, therefore, be discussed for each of the waste forms.

CHEMICAL COMPOSITION

Chemical composition is another important characteristic, since chemical potential differences will provide the major thermodynamic driving force for interactions in the geologic environment and the kinds of ions available determine the types of phases formed.

HISTORY OF WASTE FORM

The third important class of characteristics of radioactive waste affecting waste/basalt interactions includes the fuel burn-up, the age (i.e., time out of reactor) of the waste, and, in some cases, waste loading. These determine how much heat is produced by a given volume of radioactive waste. How much heat will be available in the interaction zone of the immediate repository is largely an engineering parameter. Results from our waste/basalt interaction studies may be an important factor in determining how much of a temperature rise should be allowed in the immediate repository and, thus, in the placement of waste canisters.

LEACHABILITY

Although considerable data are available under the heading of leachability, we will not be giving much attention to it in this section. Simply stated, most of the leachability measurements have been taken by the Paige (25°C), Soxhlet (95°C), or the International Atomic Energy Agency (25°C) distilled water methods⁶

and are not representative of leaching behavior under the hydrothermal conditions which are of concern in the immediate repository during the thermal period.

MISCELLANEOUS FACTORS

There are several other types of data having relevance to waste/basalt interactions. The surface area per unit mass of the waste form will certainly affect the interaction kinetics. Radiation effects, with their accompanying stored energy, will provide some activation to the interactions. However, the magnitude of this contribution should be on the order of a few tens of calories or less, whereas the thermochemical driving force for interactions will be on the order of kilocalories. It should also be pointed out that the radiation damage will be occurring during the thermal period so that much of it may be annealed out before it can contribute to waste/basalt interactions. Finally, it should be noted that solutions impinging on the waste form may be somewhat more reactive than natural hydrothermal solutions due to radiolysis of the water and other constituents.

DISCUSSION

SPENT UNREPROCESSED FUEL

Eighty percent of our experimental and theoretical efforts are presently being directed toward studying the chemical interaction of spent unprocessed fuel and basalt. These studies should be instrumental in evaluating the geochemical feasibility of storing spent unprocessed fuel in a basalt environment.

The physical and chemical data needed to evaluate the feasibility of storing unprocessed fuel in a basalt repository are limited. However, the thermodynamic state of spent unprocessed fuel should be governed largely by its phase composition. The major phase is a crystalline fluorite structure (UO_2) with fluorite-related structure fission product oxides (RE^*O_3 , CeO_2 , and some ZrO_2) in solid solution. After a survey of papers on irradiated fuel behavior, it became clear that very little else is actually known about spent unprocessed fuel crystalline phase behavior. It is widely believed that SrO and BaO react with ZrO_2 to form the perovskite structure $[(\text{Ba},\text{Sr})\text{ZrO}_3]$. There also appear to be distinct Cs-Te-rich zones. Cesium is thought to be present as a cesium molybdate and/or a cesium uranate, both of which are quite soluble in water. Spent unprocessed fuel would have a stability level in the neighborhood of the crystalline phase depicted in Figure 1 (A). Preliminary experiments seem to bear this out, since spent unprocessed fuel appears fairly unreactive relative to glass and calcine.

We anticipate that the bulk of the UO_2 -rich spent unprocessed fuel waste form would remain relatively unreactive under hydrothermal repository ambients, as long as the Eh-pH conditions keep the uranium in the tetravalent state. If the conditions become

*RE is a shorthand notation for a group of rare earth elements. As a group, they exhibit nearly identical chemical properties. This notation allows us to write a general formula which represents the group as a whole.

too oxidizing, then the uranium could be mobilized and the UO_2 would no longer be able to act as a protective matrix for the more soluble fission products and actinides.

There are data showing¹ that the composition of a mixed oxide spent unreprocessed fuel having had a burn-up of 25,000 megawatt days per metric ton of heavy fuel is approximately 97 percent UO_2 with a balance comprised of fission products and transuranic elements. In order to provide an approximate simulation of the chemistry of spent unreprocessed fuel in early preliminary experiments, we used a mixture of 95 weight percent UO_2 plus 5 weight percent PW-4b.* These were sintered in an attempt to simulate actual spent unreprocessed fuel conditions where the fission products are more typically part of a more complex compound or part of the UO_2 solid solution. No effort has been made as yet to include volatiles, especially iodine. Some of the runs in the future will also contain zircaloy and other alloys in addition to spent unreprocessed fuel and basalt.

There are leachability data on actual spent unreprocessed fuel,⁷ at 25°C. Hanford ground water, as well as deionized water, were the leachants. The relative leachability of the elements decreased in the order: $\text{Cs} > \text{Sb} > \text{Sr} + \text{Y} > \text{Pu} > \text{Cm}$ with ^{137}Cs leach rates of $\sim 5 \times 10^{-6}$ grams per centimeter per day after 21 weeks

CALCINE

Calcine is the general name for unconsolidated powder or granules made by the single-step process of evaporation (and partial decomposition) of liquid high-level waste.

*PW-4b is a simulated low sodium Purex process waste.

Calcine may have once been considered as a final waste form; but, today, calcine is typically referred to and considered as an intermediate step before consolidation to, or incorporation into, some other form.

The composition of calcines is very much a function of the reprocessing flow sheet. An ideal or "clean" calcine would have mainly fission product oxides. A flow sheet which calls for mixing the intermediate with the high-level waste stream will give a calcine with a substantial sodium and phosphate content. The efficiency of separations will determine how much uranium and plutonium remain in the waste stream. The calcine used in our studies is the "dirty"* high-uranium U. S. Department of Energy formulation PW-7a. It was formulated at one time to be typical of the high-level waste from the Nuclear Fuel Services Reprocessing Plant. Table II lists the compositions of two typical calcines: PW-4b ("Clean"); and, PW-7a ("Dirty"). PW-7a is an especially representative simulated calcine, in that it contains all of the correct chemical elements (except the radioactives: Tc; Pm; Np; Pu; Am; Cm) including the expensive elements Pd, Rh, and Ru. It was supplied to us in 1974 as PW-4b. We have converted it into a PW-7a composition by adding the appropriate amounts of extra Na, (PO_4) , Fe, and U.

The phase compositions of the calcine are important, since the crucial question of the solubility or leachability of hazardous radionuclides is principally

*"Dirty" is equivalent to high sodium; "clean" is equivalent to low sodium.

TABLE II

COMPOSITIONS OF POTENTIAL COMMERCIAL REPROCESSING
HIGH-LEVEL WASTE CALCINES
(Weight Percent)

Oxide	PW-4b ("Clean") *	PW-7a ("Dirty") *
Na ₂ O	-	9.1
P ₂ O ₅	1.6	8.3
RE ₂ O ₃ **	31.8	30.5
ZrO ₂	12.1	6.5
MoO ₃	12.6	6.8
To ₂ O ₇	3.2	1.7
RuO ₂	7.3	3.9
PdO	3.6	2.0
Cs ₂ O	7.0	3.8
Rb ₂ O	0.9	0.5
SrO	2.6	1.4
BaO	3.8	2.1
U ₃ O ₈	2.9	15.4
Rb ₂ O	0.9	0.5
TeO ₂	1.8	1.0
Fe ₂ O ₃	3.7	4.0
Cr ₂ O ₃	0.8	0.5
NiO	0.3	0.2
PuO ₂	0.2	0.1
Others	2.7	1.6

*Calculated from data in Table 2 of Mendel, et al.⁶

**RE = La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Y.

determined by the phase into which they are incorporated. Thus, Sr^{++} in SrCl_2 is over a million times more leachable than Sr^{++} in $(\text{Sr,Ca})\text{Al}_2\text{Si}_2\text{O}_8$. X-ray studies of some calcines indicate that the typical calcine is a mixture of two or three "phases" each poorly crystallized or nearly non-crystalline. As McCarthy and Davidson⁸ have shown, crystalline phases can be formed in calcines heated briefly to temperatures above $\sim 900^\circ\text{C}$. However, during these firings, much or all of the Cs, Rb, Na, Mo, Ru, and Te in the calcines are volatilized. This poor thermal stability makes it unlikely that ordinary calcines would be treated at temperatures high enough to crystallize them significantly, even though this would increase thermodynamic stability.

We have heat-treated PW-7a at 800°C for 2 hours in order to simulate the "stabilization" (i.e., elimination of most of the volatile NO_x and H_2O) step which would be used before sealing calcine canisters.¹ Even after the heating, X-ray diffraction shows that the calcine remains largely amorphous.

"Leachability" of calcine, even in room temperature water, would be expected to be high because of its high surface area per unit mass and the likely presence of water soluble "phases;" e.g., $(\text{Na,Cs})_2\text{MoO}_4$. Mendel and McElroy⁹ report that 20 to 25 percent of the constituents of a typical calcine dissolve readily on contact with water. This means that a substantial fraction of a calcine will be immediately available in solution during hydrothermal waste/basalt interaction experiments.

"Waste loading" in calcine is essentially 100 percent. However, in a canister, the amount of the low-density calcine (≈ 1 gram per cubic centimeter) would be equivalent to another product of higher density (3.0 grams per cubic centimeter) with 33 weight percent loading.

GLASS

Development of vitrification processes for solidification of high-level waste began more than two decades ago in the United States and abroad. As far back as ten years ago, a pilot-scale hot demonstration of phosphate and borosilicate glass processing was under way at the Hanford site (the Waste Solidification Engineering Prototypes Program). In the future, Battelle-Northwest will be demonstrating in-can solidification by vitrification of actual high-level waste made by onsite reprocessing of spent fuel. Clearly, glass was the waste form closest to utilization for the near term and, for this reason, it was previously given the greatest consideration in our waste/basalt interactions program.

It is widely appreciated that glass is in an excess free energy state compared to the assemblage of equilibrium crystalline phases of the same bulk composition. It is for this reason that high-level waste glasses are subject to "devitrification" (partial crystallization) on slow cooling and when held in the temperature range of 500 to 800°C. The Battelle-Northwest Glass 72-68 has been shown to devitrify into $(\text{Ca}, \text{Sr}, \text{Ba})\text{MoO}_4$, Zn_2SiO_4 , $(\text{Zn}, \text{Ni})(\text{Fe}, \text{Cr})_2\text{O}_4$, and $\text{Ca}_2\text{RE}_8^*(\text{SiO}_4)_6\text{O}_2$ after these

*See Table III.

TABLE III

COMPOSITION OF BATTELLE-NORTHWEST GLASS 76-68*

Oxide	Wt. %	Oxide	Wt. %	Oxide	Wt. %
SiO ₂	39.8	MoO ₃	2.3	P ₂ O ₅	0.5
Na ₂ O	12.5	CaO	2.0	Cr ₂ O ₃	0.4
Fe ₂ O ₃	9.8	ZrO ₂	1.8	SrO	0.4
B ₂ O ₃	9.5	CeO ₂	1.2	TeO ₂	0.3
ZnO	5.0	RuO ₂	1.1	NiO	0.2
U ₃ O ₈	4.6	Cs ₂ O	1.0	Rh ₂ O ₃	0.2
RE ₂ O ₃ **	3.4	BaO	0.6	Rb ₂ O	0.1
TiO ₂	3.0	PdO	0.5	Others	0.1

*Modified from a table provided by D. Bradley, Battelle-Northwest.

**RE = La, Pr, Nd, Sm, Eu, Gd, Y.

thermal treatments. In addition, crystalline RuO_2 , $(\text{Ce} \dots)\text{O}_2$ and Pd were also present in the freshly formed glass as undissolved components.⁶

Investigators have observed hitherto unreported glass-in-glass phase separation by transmission electron microscopy. Thus, high-level waste "glass" falls between glass and crystal in Figure 1 (A) and (B). Thus, we would expect glass to be intermediate in reactivity between calcine and the more completely crystallized supercalcine and spent unprocessed fuel during our waste/basalt interactions studies.

The specific glass we have chosen in our interactions studies is exactly the same specimen being used in the source term characterization task of the Office of Waste Isolation/Battelle-Northwest/Waste Isolation Safety Assessment Program. Its code is 76-68 and the specimen was provided by J. E. Mendel of Battelle-Northwest. With regard to the above discussion on devitrification, it should be noted that 76-68 shows significantly less devitrification than 72-68.¹⁰ Only Ru, RuO_2 , two spinel phases, and $(\text{U}, \text{Ce} \dots)\text{O}_{2+x}$ have been noted to date in heat-treated 76-68.

The composition of Glass 76-68 is given in Table III. The waste composition (PW-8a) used to prepare Glass 76-68 was calculated to be typical of one of the high-level wastes to have been generated by the Nuclear Fuel Services Reprocessing Plant. PW-8a is similar in composition to PW-7a (Table II), except that it has approximately 2 times the sodium and approximately 9 times the iron.

PW-8a was combined with a glass-making frit, which can be described as a soda-lime-zinc-titanium borosilicate. It should be noted that this simulated high-level waste glass composition (76-68) is as representative as it can be without including the radioactive elements. In Table III, the oxides have been listed in order of decreasing concentration. The molybdenum oxide is approximately 20 percent greater than it would be in actual high-level waste, because Mo has been used as a "stand-in" for Tc.

SUPERCALCINE

McCarthy, et al.,¹¹⁻¹³ have described the first successful supercalcine formulations. The basic premise of this tailor-made ceramic is that modifications can be made to high-level liquid waste compositions through the addition of selected liquid additives so that, when the liquid is calcined and given additional heat treatment, an assemblage of refractory and leach-resistant phases is crystallized. The name "supercalcine" was coined to indicate a common processing operation with "calcine." An important component of this research has been the collaboration with Battelle-Northwest where engineering-scale "cold" demonstrations and product characterization have been performed.

To date, McCarthy and his co-workers have succeeded in the development of effective formulations for converting both "clean" and "dirty" high-level liquid waste (see Table II) into compatible assemblages of refractory and leach-resistant phases. Table IV lists these phases and structure types. The mix of phases differs with the waste composition. Additions of nitrates of Ca, Sr, and Al, plus soluble forms of silica, are made to the

TABLE IV

FIXATION PHASES FOR HIGH-LEVEL WASTE
CONSTITUENTS IN SUPERCALCINE

Constituent	Fixation Phase	Structure Type
Cs,Rb.....	$(\text{Cs,Rb})\text{AlSi}_2\text{O}_6$	Pollucite
Sr,Na,Mo.....	$(\text{Ca,Sr})_2[\text{NaAlSiO}_4]_6(\text{MoO}_4)_2$	Sodalite
Sr,Ba,Mo.....	$(\text{Ca,Sr,Ba})\text{MoO}_4$	Scheelite
Sr,RE,* PO ₄	REPO ₄	Monazite
	$(\text{Ca,Sr})_2\text{RE}_8[\text{SiO}_4]_6\text{O}_2$	Apatite
Ce,U,Zr.....	$(\text{Ce,U,Zr})\text{O}_{2+x}$	Fluorite
	$(\text{Zr,Ce})\text{O}_2$	
Fe,Ni,Cr.....	$(\text{Fe,Ni})(\text{Fe,Cr})_2\text{O}_4$	Spinel Corundum
	$(\text{Fe,Cr})_2\text{O}_3$	
Ru.....	RuO_2	Rutile

*La, Pr, Nd, Pm, Sm, Eu, Cd, Y (and probably Am, Cm).

high-level liquid wastes. These additions give dilution by only 20 to 40 weight percent of unmodified high-level waste calcine. To date, three engineering-scale demonstrations of supercalcine preparation by spray calcination have been performed at Battelle-Northwest. Spray supercalcine is X-ray amorphous and must be heated briefly above 950°C to "develop" the assemblage of crystalline phases. Reference 1 states that "if an unconsolidated calcine continues to be an acceptable waste form, supercalcine formulation concepts can be introduced into flowsheets immediately which would improve the stability and insolubility of some of the radioactive waste constituents."

Current emphasis is on developing monolithic forms of supercalcine and recent tests of 5 to 10 millimeter spherical pellets encased in a metal matrix have been very encouraging.

The free energy state of supercalcine in-canister is not at the exact minimum as might be expected from its definition. One reason is the structural disorder in certain supercalcine phases that is introduced by radiation and transmutation of effects. A second reason is because excess additives are included in each formulation to allow for compositional variation in the realistic high-level liquid waste streams. Thus, enough excess Al + Si is added to crystallize twice the Cs nominally present in a reprocessing plant's high-level liquid waste composition. Much of this excess alumina plus silica remains as a non-crystalline phase after the brief crystallization heat treatment and

keeps a real supercalcine from attaining minimum free energy for its particular composition. However, it has been established that the 94 to 97 weight percent of the supercalcine product that is crystalline is in "effective" equilibrium when formed. Thus, one formulation (SPC-2) has been fired for weeks at 900°C without modifying the assemblage of nine compatible crystalline phases.

The specific formulation being used in our reconnaissance waste/basalt interactions studies is SPC-2. It was prepared according to McCarthy's formulation¹⁴ on the spray calciner at Battelle-Northwest and crystallized by firing at 1,125°C for 2 to 4 hours. The crystalline phases and their shorthand notation in SPC-2 are:

$\text{Ca}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$	$[\text{A}_{\text{ss}}]$	$(\text{Cs}, \text{Rb}, \text{Na})\text{AlSi}_2\text{O}_6$	$[\text{P}]$
REPO_4	$[\text{M}_{\text{ss}}]$	$(\text{Ce}, \text{Zr} \dots)\text{O}_2$	$[\text{F}_{\text{ss}}]$
Tetragonal- ZrO_2	$[\text{T}_{\text{ss}}]$	$(\text{Fe}, \text{Cr})_2\text{O}_3$	$[(\text{Fe}_2\text{O}_3)_{\text{ss}}]$
$(\text{Ca}, \text{Sr}, \text{Ba})\text{MoO}_4$	$[\text{S}_{\text{ss}}]$	$(\text{Ni}, \text{Fe})(\text{Fe}, \text{Cr})_2\text{O}_4$	$[\text{SP}_{\text{ss}}]$

The complete composition of SPC-2 oxides is given in Table V and a portion of an X-ray diffractogram of crystallized SPC is shown in Figure 2.

It has been stated that supercalcine phases are in effective equilibrium when formed and at the temperature expected in-canister for stored high-level waste (<800°C). More relevant in the context of our waste/basalt interactions studies is whether these phases will be in equilibrium with each other and with the surrounding rocks under the hydrothermal conditions which could be typical of a geologic repository. Our expectation is that some phases

TABLE V
COMPOSITION OF SUPERCALCINE SPC-2

Ion	Molarity	Oxide	Grams Oxide Per Liter of Calcined SPC-2	Weight Percent Oxide
<u>FROM THE MODIFIED PW-7 WASTE:</u>				
Ce	0.161	CeO ₂	27.7	16.3 (12.7) ¹
Zr	0.106	ZrO ₂	13.0	7.6 (5.9)
RE ²	0.102 ²	RE ₂ O ₃	17.0	10.0 (7.8)
Fe	0.100	Fe ₂ O ₃	8.0	4.7 (3.7)
[PO ₄]	0.100	P ₂ O ₅	7.1	4.2 (3.2)
Mo	0.095	MoO ₃	13.7	8.0 (6.3)
La	0.094	La ₂ O ₃	15.3	9.0 (7.0)
Cs	0.054	Cs ₂ O	7.6	4.5 (3.5)
Sr	0.027	SrO	2.8	1.6 (1.3)
Ba	0.027	BaO	4.1	2.4 (1.9)
Cr	0.012	Cr ₂ O ₃	0.9	0.5 (0.4)
Rb	0.010	Rb ₂ O	0.9	0.5 (0.4)
Ma	0.010	Na ₂ O	0.3	0.2 (0.1)
Ru ³	0.006	RuO ₂	0.8	0.5 (0.4)
Mi	0.005	NiO	0.4	0.2 (0.2)
Cd	0.002	CdO	0.3	0.2 (0.1)
<u>SUPERCALCINE ADDITIVES:</u>				
Si	0.539	SiO ₂	32.4	19.1 (14.8)
Ca	0.150	CaO	8.4	4.9 (3.8)
Al	0.148	Al ₂ O ₃	7.5	4.4 (3.4)
Sr	0.020	SrO	2.1	1.2 (1.0)
			170.4	100.0
(70.5 percent waste loading)				
<u>OTHER WASTE CONSTITUENTS:</u> ⁴				
U(Pu,Np)	0.1195	U ₃ O ₈	33.6	(15.5)
Ru ³	0.053	RuO ₂	7.1	(3.2)
Pd	0.032	PdO	3.9	(1.8)
Te	0.012	TeO ₂	1.9	(0.9)
Rh	0.010	Rh ₂ O ₃	1.3	(0.6)
Ag	0.002	AgO	0.3	(0.1)
			218.5	100.0
(76.9 percent waste loading)				

¹Value in parentheses is the weight percent of the oxide after addition of the appropriate amounts of U, Ru, Pd, Te, Rh, Ag.

²RE = 0.061 Nd + 0.019 Pr + 0.011 Sm + 0.007 Gd + 0.003 Y (Note: 0.002 RE is a stand-in for Am+Cm).

³Ru concentration in the spray supercalcine SPC was 10 percent of the actual PW-7 value of 0.059 M. The addition of the remaining 0.053 M was made after calculation.

⁴These constituents were not included in the large batch of SPC-2 because of their expense or radioactivity. None require fixation additives. The only PW-7 constituent not included above is Tc.

FIGURE 2

PORTION OF THE X-RAY DIFFRACTOGRAM OF SUPERCALCINE SPC-2

(The shorthand notations of the crystalline phases are explained in the text.)

will be and some will not. Many of the mineral phases listed in Table V are found in nature in hydrothermally formed igneous rocks. Thus, it is very likely that these minerals will be stable in hydrothermal environments at temperatures approximating their crystallization temperatures. Pollucite ($\text{CsAlSi}_2\text{O}_6$), for example, is only formed in nature under hydrothermal conditions. Indeed, we would even expect pollucite to be a hydrothermal interaction product when the wastes are as reactive as calcine or glass (and, thus, readily give up their Cs) and when the rocks contain alumina and silica. Furthermore, according to the earlier discussion on reactivity of crystalline waste forms, those super-calcine crystalline phases that are not in equilibrium in the hydrothermal geologic environment would be expected to react quite slowly with any solutions.

CONCLUSIONS

Those physical and chemical factors which appear to have bearing upon the stability and/or reactivity of various radioactive wastes in contact with basalt under repository conditions have been evaluated. It is apparent from the tests that each class of waste form has unique properties which may or may not be detrimental to the concept of final storage of radioactive waste in basalt. For example, our measure of potential reactivity (the excess free energy) predicts that the most reactive of the waste forms would be calcines and the most stable waste form would be a crystalline assemblage such as spent unprocessed fuel (see Figure 1).

The importance of the excess free energy and other factors we have discussed in the tests is obvious; they form a foundation for future laboratory evaluation

of waste/basalt interactions for each of the waste form/basalt pairs. In other words, the waste form data themselves are no longer the major issue. Instead, we have a task with a broader scope -- to study each of the potential interactions of radioactive waste and basalt as a single system under repository conditions.

ACKNOWLEDGMENTS

The authors would like to acknowledge the assistance of Mr. W. A. Ross, Battelle-Northwest, and Dr. R. L. Gibby, Hanford Engineering Development Laboratory, in adapting Table I for this report.

We would also like to acknowledge the efforts of Dr. J. A. Apps, Lawrence Berkeley Laboratory, in reviewing the manuscript in its earliest stages.

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