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Stabilization of Coal Wastes by Crystallization

R. J. Lauf
J. I. Federer
V. J. Tennery

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Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A03 Microfiche A01

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ORNL/TM-7071
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Contract No. W-7405-eng-26

METALS AND CERAMICS DIVISION

STABILIZATION OF COAL WASTES BY CRYSTALLIZATION

R. J. Lauf, J. I. Federer, and V. J. Tennery

Date Published: March 1980

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STABILIZATION OF COAL WASTES BY CRYSTALLIZATION

R. J. Lauf, J. I. Federer, and V. J. Tennery

ABSTRACT

All bituminous coals contain minerals, which upon combustion result in residual matter, which is called either ash or slag, depending primarily upon its physical form. Fine particulate waste is ash, while more massive waste is slag. Many coals contain impurity elements that can be very detrimental to humans, and the disposition of these elements in the ash or slag is of growing interest from an environmental point of view. Numerous conversion processes are now being investigated on a national scale to determine the engineering and economic potential for producing hydrocarbon gases or liquids from coal. An important aspect of this issue is the nature of the residual matter from the conversion process and the prospects for its safe disposal.

The ash from the Hygas process, an experimental method to produce high-Btu gas from coal, was studied to determine its crystallization properties when cooled from the melt. The Hygas ash produced a melt primarily Al_2O_3 - SiO_2 - Fe_2O_3 with a low alkali and alkaline earth content and a small amount of other impurities.

When this material was cooled at various rates from 1400°C after different hold times at temperature, the only significant phase that crystallized from the melt was iron oxide in the form of hematite, Fe_2O_3 , plus some magnetite, Fe_3O_4 . The lattice parameters of the Fe_2O_3 were in all cases smaller than the standard values by a few percent because of incorporation of titanium and some aluminum from the melt. Decreasing the cooling rate after melting at 1400°C increased the amount of Fe_2O_3 crystal growth but did not result in any silicate crystal phases. Titanium originally present in the melted slag at 0.3 wt % partitioned preferentially to the Fe_2O_3 crystals.

Synthetic slag compositions containing from 9 to 31 wt % Na_2O were prepared to reduce the refractoriness of the Hygas slag, and these additions reduced the temperature for homogeneous melt development from about 1400°C to about 1100°C . These compositions were doped with up to 0.5 wt % Pb, Se, and Te to determine how these potentially harmful elements partitioned between the glass and crystal phases during cooling. Additionally, Soxhlet leaching tests were performed on these crystallized simulant slags to determine the effect of the sodium oxide additions on leach extraction. Fluxing of the Hygas slag with sodium oxide additions increased the stability

of the siliceous glass phase, but the only major crystalline phase developed was again Fe_2O_3 . Extraction in boiling neutral water showed that use of sodium as a flux increases the leachability of Pb, Se, and Te from the cooled slag. Rapid quenching of the molten sodium-modified slag in water reduced the tellurium extraction by a factor of about 4 compared with results from furnace-cooled compositions. These tentative results show that simple compositional alterations to wastes such as Hygas ash using Na_2O to reduce the temperature required to conveniently work the slag can increase the leachability of Pb, Se, and Te and that the cooling history of the melt can significantly affect the ease of extraction of some trace elements.

INTRODUCTION

Coal gasification processes are presently expected to meet a significant portion of U.S. energy needs later in this century. These processes will produce large quantities of solid wastes (slag and ash) as by-products. The wastes include mineral matter from the coal as well as unreacted carbonaceous material. An important consideration in the final commercialization of one or more candidate processes will be the utilization or disposal of these solid wastes in an environmentally acceptable way. An ongoing program at ORNL is determining the possible environmental impact of disposal by burial of slag and ash from selected coal conversion processes. The leaching and subsequent movement of detrimental trace elements (e.g., Pb, Se, Te, As, etc.) from wastes to surrounding soils and ground water are being studied to determine if they can safely be used as landfills in their original form. Our principal objective was to evaluate means of stabilizing solid wastes from one candidate coal conversion process.

Ash and slags from most coal conversion processes contain amorphous siliceous materials, which are thermodynamically unstable relative to a crystalline solid of the same composition. These glassy materials can be corroded and leached by ground waters if the wastes are stored or buried in soils. A major objective of our work is to study the possible stabilization of these wastes by crystallization. This requires developing an understanding of the crystallization path, determining

developed phases and partitioning of harmful elements among the various phases, and evaluating leaching characteristics.

Solidification studies included not only as-received ash (Hygas Process*) but also simulated ash mixtures. Some mixtures contained additions of biologically harmful trace elements (Pb, Se, and Te), while others contained additives (9–31% Na_2O) to lower the liquidus temperature of the slag or ash. Various solidification rates and heat treatments were used, and the resulting solids were examined both by microscope and by x-ray diffraction. Powdered specimens were also characterized by leaching using the Soxhlet extraction method.

It became obvious early that a detailed understanding of the crystallization behavior of the ash when cooled from high temperatures was of central importance to the assessment of the potential for melt modification to reduce the aqueous leachability of certain elements. Because of the relatively complex melt compositions involved, it appeared possible that there were several alternatives for the crystallization path. Furthermore, it was necessary to clearly identify the crystallization behavior of the candidate ash. Therefore, we gave much attention to developing a clear understanding of the sensitivity of the melt to producing various crystalline phases as a function of composition and cooling history.

EXPERIMENTAL PROCEDURES AND MATERIALS

As-Received Hygas Ash

The starting material was an aqueous slurry containing about 5 wt % solids. After drying the solids formed a black, granular material, which was about 63 wt % C. The carbonaceous phase was oxidized at about 800°C in air, and the resulting material was quantitatively analyzed. The analyses are presented in Tables 1 and 2.

The major crystallizing phases were determined by x-ray diffraction. These will be discussed in detail later.

*Institute of Gas Technology, Chicago, Illinois.

Table 1. Major Constituents
of Hygas Ash

Element	Content (wt %)	Oxide Equivalent	Content (wt %)
Al	7.2	Al ₂ O ₃	14.3
Si	23.6	SiO ₂	53.7
Fe	15.8	Fe ₂ O ₃	24.7
Ca	2.1	CaO	3.1
K	1.1	K ₂ O	1.5
Mg	1.0	MgO	1.8
Na	0.6	Na ₂ O	0.8

Table 2. Major Impurities
in Hygas Ash

Content (ppm) ^a					
B	100	Mo	50	Ti	3000
Ba	500	Nb	10	Tl	30
Co	30	Ni	200	V	200
Cr	100	P	300	Zn	200
Cu	100	Pb	100	Zr	200
Ga	100	Rb	400	Br	3
Ge	50	Sc	10	Cl	50
Mn	500	Sr	300	S	2000
Total Rare Earths		340			

^aSemiquantitative analysis
(spark source mass spectroscopy).
Values are accurate within a factor
of 2.

Melting and Heat Treatments

Powdered specimens were compressed into pellets of about 1 g and were melted in platinum crucibles. Melting was generally accomplished at 1400°C, although it will be seen later that some solid Fe₂O₃ was apparently in the melt at that temperature. The melted slag samples were then cooled at various rates by

1. ice water quenching, which resulted in a primarily glassy product;
2. air cooling, which yielded a partly crystallized structure with much glass; and
3. furnace cooling, which produced a fully dendritic ingot structure with some glass remaining in the interdendritic regions.

To investigate the possibility of devitrifying a glassy slag, some water-quenched specimens were annealed at 950°C in air for various times.

Preparation of Doped Slags

To examine the behavior of certain toxic elements in the waste material during crystallization and leaching, ash specimens were melted with additions of Pb, Se, and Te. Various compounds of these elements were used in the batch to minimize volatilization of the elements of interest. Lead was successfully added as PbSO_4 (anglesite), selenium was added as PbSe , and tellurium was added as Na_2TeO_4 . These phases lost their identity during the melting process.

Preparation of Synthetic Slags

The Hygas ash melted to a reasonably homogeneous material at about 1400°C. Since melting large amounts of this material for stabilization processing would be very energy intensive, we investigated the possibility of altering the composition to lower the solidus and/or liquidus temperatures. Two synthetic slags were prepared on the basis of known melting points of several familiar oxides. Table 3 shows the reference compositions used to develop the target synthetic slag compositions shown in Table 4. Reference composition A in Table 3 is the eutectic between albite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) and fayalite ($2\text{FeO} \cdot \text{SiO}_2$), which melts at 1050°C at about 16 wt % fayalite.¹ Synthetic slag HA-16 was based on this eutectic. Reference compositions B and C are ternary eutectics in

Table 3. Reference Compositions Used to Develop Synthetic Slags

Reference Composition	Melting Point (°C)	Equivalent Oxide Content, wt %			
		Al ₂ O ₃	FeO or Fe ₂ O ₃	Na ₂ O	SiO ₂
A. Na ₂ O·Al ₂ O ₃ ·6SiO ₂ - 2FeO·SiO ₂ eutectic	1050	16.4	11.3 ^a	9.9	62.4
B. Al ₂ O ₃ - Na ₂ O - SiO ₂ ternary eutectic	915	18.7		37.4	25.6
C. Fe ₂ O ₃ - Na ₂ O - SiO ₂ ternary eutectic	809		28.8 ^b	25.6	45.4
D. Combination of B and C	800-900 ^c	9.4	14.4 ^b	31.6	44.7

^aFeO.^bFe₂O₃.^cEstimated melting range.

Table 4. Compositions of Synthetic Slags from Reference Compositions

Reference Composition ^a	Synthetic Slag	Melting Point (°C)	Equivalent Oxide Content, wt %						Dopants Content (wt %) ^b		
			Al ₂ O ₃ ^c	CaO	FeO or Fe ₂ O ₃	K ₂ O ^d	Na ₂ O ^d	SiO ₂	Pb ^e	Se ^f	Te ^g
A	HA-16	1050	16.1	1.7	11.1	0.8	8.9	61.3	0.5	0.02	0.3
D	HA-17	800-900 ^h	10.3	2.3	13.1	1.1	30.7	42.5	0.4	0.06	0.3
D	HA-21	800-900 ^h	10.3	2.3	13.1	1.1	30.7	42.5	0.4	0.02	0.2
D	HA-22	800-900 ^h	10.3	2.3	13.1	1.1	30.7	42.5	0.4	0.02	0.1

^aLetters refer to reference compositions in Table 3.^bNumbers are actual concentrations determined by chemical analyses. Intended content was 0.5 wt % in all cases.^cContained in the original mixture as mullite, 3Al₂O₃·2SiO₂.^dContained in the original mixture as carbonates.^eAdded as PbO except for HA-22, where it was added as PbSe.^fAdded as an element except for HA-22, where it was added as EtSe.^gAdded as an element except for HA-22, where it was added as Na₂TeO·2H₂O.^hEstimated melting range.

the alumina-soda-silica^{2,3} and hematite-soda-silica^{2,4} systems, respectively. Synthetic slags HA-17, -21, and -22 were based on a combination of these two eutectics and were expected to melt in the range 800 to 900°C.

The synthetic slags were prepared from oxides and carbonates of the constituents shown in Table 3 along with small amounts of CaO and K₂O (the latter as K₂CO₃) to approximate the composition of the Hygas ash. The Na₂O and K₂O were derived from the carbonates by in situ decomposition. An advantage of this procedure was formation of liquid sodium carbonate at 851°C, a temperature well below the melting point of any of the oxides. This liquid perhaps hastened the dissolution process needed to form a homogeneous melt. A disadvantage of carbonate use was the evolution of CO₂, which can cause the molten material to bubble and overflow the crucible. This situation was controlled by limiting the rate of heating of the melt.

Synthetic slags were doped with Pb, Se, and Te in the forms of PbO, Se and Te as elements, PbSe, and Na₂TeO₄·2H₂O. Melting was accomplished in Alundum (Al₂O₃) crucibles in air.

X-Ray Diffraction

A sample size about 12 by 25 by 1.5 mm of -100 mesh powder (<150 μm) was used in a Norelco diffractometer. If the samples were mostly glass, as expected, this arrangement enhances the intensities of small amounts of crystalline phases better than the more standard thinner samples, such as coated fibers, filled capillaries, or thin layers on glass slides. The incident x-ray beam was generated by a copper target tube, and the scan speed in 2θ was 0.25°/min. The diffracted beam was monochromated by a singly bent graphite crystal tuned for Cu Kα radiation (λ = 0.154178 nm). The monochromated beam was collected in a proportional counter, which recorded the data on paper tape. The data were then plotted graphically with a Calcomp plotter. Phases were identified by comparing lattice spacings shown in the diffractograms with those of known compounds.

Soxhlet Extraction

To compare the leaching characteristics of the different slag samples, a standard test procedure was used. The Soxhlet extraction test apparatus is shown schematically in Fig. 1. The test consists of bringing the powdered sample into contact with a solvent (e.g., water), which is recycled to become enriched in solutes. This is accomplished by a continuous distillation-condensation process. After sufficient time has elapsed, the liquid is quantitatively analyzed for the trace elements of interest. The assumption is that a sample that yields more lead, for instance, than another sample in the Soxhlet test would likewise yield more lead to the soil if the slag were buried. By the addition of an appropriate quantity of acid to the starting solution, one can lower the pH of the solvent in contact with the sample and compare the leaching rates as a function of the pH of the solution. This is useful for examining the possible consequences if buried wastes are infiltrated by acidic ground waters. Samples of slags after various heat treatments were crushed to -325 mesh ($<45\ \mu\text{m}$), and about 1 g of each powder was used for the extraction tests.

Summary

The composition and slag sample treatments examined in this study are summarized in Table 5. For each sample the conditions of melting and solidification are given along with heat treatments, if any, and any compositional additions.

RESULTS AND DISCUSSION

Melting and Crystallization of Hygas Ash

Phase Identification

The major crystalline phases in the unmelted ash (after burning off the carbonaceous fraction) were determined by x-ray diffraction. The

Fig. 1. Soxhlet Extraction Test Apparatus.

Table 5. Summary of Ash Compositions and Treatments Examined

Sample	Composition	Melting		Cooling Method ^a	Heat Treatment	
		Temperature (°C)	Time (h)		Temperature (°C)	Time (h)
HA-1	Hygas Ash				800	24
HA-3	Hygas Ash	1400	1	FC		
HA-4, -2	Hygas Ash	1400	1	AC		
HA-11, -23	Hygas Ash	1400	1	WQ		
HA-12	Hygas Ash	1400	18	WQ		
HA-13	Hygas Ash	1400	18	AC		
HA-14	Hygas Ash	1400	18	FC		
HA-24	Hygas Ash	1400	2	WQ	950	2
HA-25	Hygas Ash	1400	2	WQ	950	24
HA-26	Hygas Ash	1400	2	WQ	950	100
HA-18	Hygas Ash plus 1% PbO ^b	1400	2	WQ		
HA-19	Hygas Ash plus 1% PbO ^b	1400	2	AC		
HA-20	Hygas Ash plus 1% PbO ^b	1400	2	FC		
HA-6	Simulated Hygas Ash ^c plus 0.5 wt % each PbO, Se, and Te	1425	2	FC		
HA-16	Synthetic Slag ^d	1200	18	FC		
HA-17	Synthetic Slag ^d	1025	18	FC		
HA-21	Synthetic Slag ^d	1100	3	FC		
HA-22	Synthetic Slag ^d	1100	3	WQ		

^aFC = furnace cooled, AC = air cooled, and WQ = ice water quenched.

^bNominal, as PbSO₄.

^cComposition given in Table 1, duplicated by using oxides.

^dCompositions are given in Table 4.

diffraction pattern is shown in Fig. 2, from which it can be seen that the important crystalline phases are α -quartz (SiO_2) and hematite (Fe_2O_3). Some glassy material is also present, indicated by the diffuse intensity or diffraction halo in the 2θ range from 15 to 35° .

After melting at 1400°C and air cooling, the quartz had disappeared from sample HA-2 and the material consisted primarily of a glassy phase, which is evidenced by the increased halo intensity. The Fe_2O_3 remains a major phase, as seen in Fig. 3. Some magnetite (Fe_3O_4) forms as a result of this treatment, although the total amount is not large. When the sample was held for several hours in the molten state at 1400°C , the solid inclusions of Fe_2O_3 partially transformed into Fe_3O_4 . This is not unexpected since these two phases should coexist at 1400°C in air.⁵

After furnace cooling, sample HA-3 contained relatively more Fe_3O_4 and less Fe_2O_3 , as shown in Fig. 4. No crystalline silicate phases appear to form, and we conclude that solidification of this gasifier ash proceeds by the rejection of iron oxides from the melt. The Fe_2O_3 lattice parameters determined by x-ray diffraction in this work are all smaller than the previously documented values⁶ by a few percent. We will show later that Fe_2O_3 crystals in this material contain considerable amounts of titanium and possibly some aluminum,⁷ which could cause a slight contraction in the lattice spacings.

Optical Ceramography

The structures of slags HA-11 and -12 that were water quenched in platinum crucibles from 1400°C are shown in Fig. 5. The structure consisted of blocky crystals surrounded by a glassy matrix. The blocky crystals are optically active when viewed with polarized light, and this agrees with the x-ray diffraction results that the phase is rhombohedral Fe_2O_3 (hematite).

A comparison of Fig. 5(a) and (b) shows the crystal growth that occurs when the melt is held several hours at 1400°C . The blocky crystals become much larger, and several acquire planar surfaces. The presence of crystal faces as well as the optical anisotropy confirm that this phase is a crystalline solid in the melt at 1400°C , rather than a second (immiscible) liquid phase.

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Fig. 2. The X-Ray Diffraction Pattern for As-Received Hygas Ash After Burning Off Carbonaceous Material. Phases are quartz (*), hematite (Fe_2O_3) (†), magnetite (Fe_3O_4) (▼), and glass.

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Fig. 3. The X-Ray Diffraction Pattern for Sample HA-2 Melted at 1400°C for 1 h and Air Cooled. Phases are hematite (Fe₂O₃)(+), magnetite (Fe₃O₄)(▼), and glass.

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Fig. 4. The X-Ray Diffraction Pattern for Sample HA-3 Melted at 1400°C for 1 h and Furnace Cooled. Phases are hematite (Fe_2O_3) (†), magnetite (Fe_3O_4) (▼), and glass.

Fig. 5. Slag Samples Water Quenched from 1400°C. (a) HA-11 held for 1 h at 1400°C before cooling. (b) HA-12 held for 18 h at 1400°C before cooling. Note the increase in crystal size.

The structures resulting from air cooling of slag samples in platinum crucibles from 1400°C are shown in Fig. 6. As in the previous figure, Fig. 6(a) and (b) shows the samples that were held at 1400°C for 1 h and 18 h, respectively, before air cooling. In both samples the matrix is still mostly glass, but small needle-like dendrites are also present. Nucleation of the dendrites occurs at the melt surface along the crucible walls and around the primary Fe_2O_3 particles. This needle-like phase is also Fe_2O_3 , and the strong nucleation at the large particles will be seen more clearly later in one of the doped slags (Fig. 11).

The microstructures of furnace cooled slags HA-3 and -14 are shown in Fig. 7(a) and (b). Here the secondary Fe_2O_3 dendrites cover the entire polished sample cross section, with glass remaining in the interdendritic regions. Some dendrites appear to share a common orientation with the primary particles, further reinforcing the conclusion that the dendrites are also Fe_2O_3 .

Electron Microprobe

The results of electron microprobe examination of the air-cooled sample HA-4 are shown in Figs. 8 and 9. The blocky particles are rich in Fe and Ti and contain virtually no Si, Ca, or K. These latter elements are segregated into the glassy phase, which also contains considerable iron and titanium in solution.

The furnace-cooled sample HA-3 is shown in Fig. 10. Comparison of the backscattered electron image [Fig. 10(a)] with the x-ray images for iron and silicon [Fig. 10(b) and (c)] reveals that the dendrites are iron-rich and silicon-poor. This is further evidence that at 1400°C the glassy phase in this material is saturated with respect to iron oxide, and solidification occurs by further rejection of Fe_2O_3 from the melt. It is interesting to note the small region around the primary Fe_2O_3 particles in which there is a smaller concentration of dendrites. The probable explanation for this phenomenon is that in the first stage of solidification, iron oxide particles precipitate onto the surfaces of the primary particles. As the temperature decreases and ionic mobility

100 μm

Fig. 6. Slag Samples Air Cooled from 1400°C. (a) HA-4 held for 1 h at 1400°C before cooling. (b) HA-13 held for 18 h at 1400°C before cooling.

Fig. 7. Slag Samples Furnace Cooled from 1400°C. (a) HA-3 held for 1 h at 1400°C before cooling. (b) HA-14 held for 18 h at 1400°C before cooling.

Fig. 8. Electron Microprobe Displays of Air-Cooled Slag Specimen HA-4. (a) Backscattered electron image. (b) Fe $K\alpha$. (c) Ti $K\alpha$.

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Fig. 9. Electron Microprobe Displays of Air-Cooled Slag Specimen HA-4. (a) Si $K\alpha$. (b) Ca $K\alpha$. (c) K $K\alpha$.

Fig. 10. Electron Microprobe Displays of Furnace-Cooled Slag Specimen HA-3. (a) Backscattered electron image. (b) Fe $K\alpha$. (c) Si $K\alpha$.

in the glass decreases, the planar crystal growth mechanism ceases and dendritic growth becomes predominant. Because of the initial deposition of Fe_2O_3 onto the primary crystals, there is a local depletion of iron oxide in the glass immediately adjacent to them, and hence fewer Fe_2O_3 dendrites form in these regions.

Doped Slags

Phase Identification

The x-ray diffraction patterns for samples HA 6, -18, -19, and -20 indicated that the only identifiable phases in the doped slags are glass, hematite, and magnetite. No diffraction peaks were present for these samples that were not present for the undoped specimens. Also, the relative amount of glass present after a given cooling history is about the same in both the doped and undoped slags.

Optical Ceramography

The general microstructures of the doped slags were nearly identical to those of the undoped slags under similar solidification conditions. Figure 11 shows the microstructure of the air-cooled specimen HA-19, which contains some lead (added as PbSO_4). Comparison of the bright field micrograph [Fig. 11(a)] with the polarized-light micrograph [Fig. 11(b)] clearly shows the nucleation of the fine dendritic phase around the primary Fe_2O_3 particles.

The microstructure of furnace-cooled specimen HA-6 is shown in Fig. 12. This sample is interesting in that it was made by mixing metal oxides to duplicate the Hygas ash composition shown in Table 1, followed by the addition of PbO , Se, and Te. There are no large primary Fe_2O_3 particles in this specimen. The hematite still formed dendrites, which were slightly coarser than those in the other samples [HA-3 in Fig. 7(a)]. Also visible in Fig. 12 are gray particles surrounded by a crystalline reaction zone. These are silica grains that did not completely dissolve in the melt. Such artifacts are often seen in ceramic materials and are referred to as "silica relics."⁸

Fig. 11. Air-Cooled (doped with PbSO_4) Specimen HA-19.
(a) Bright field. (b) Polarized light, showing nucleating
of fine dendritic phase around primary particles.

Fig. 12. Furnace-Cooled Slag Specimen HA-6, Showing Iron Oxide Dendrites (D) and Silica Relics (R).

Specimen HA-6 is shown in Fig. 13 at somewhat higher magnification, and the bright field micrograph [Fig. 13(a)] shows the structure of the individual Fe_2O_3 crystallites and dendrites. Under polarized light [Fig. 13(b)] it can be seen that some of the hematite crystals are surrounded by a narrow rim of more finely crystalline material. This appears to be an iron oxide also and could be the result of crystallization at lower temperatures where the melt would be more viscous.

We can conclude from x-ray data and optical microscopy that small additions of trace elements ($<1\%$) do not affect the overall course of crystallization of this type of melt or the final distribution of phases.

Electron Microprobe

The results of microprobe examination of the doped slags are typified in Fig. 14. The backscattered electron image shows the dendrite structure at a magnification of about 300 $\times$. The x-ray intensity images again show the dendrites to be iron-rich, while poor in silicon and alkali metals. The bulk concentrations of Pb, Se, and Te were not high enough to be detected by the microprobe. Since there were no small segregations of these elements, it is probable that they are uniformly distributed throughout the glassy phase. It is unlikely that such low-melting components would be included in the high-melting-point iron-rich oxide phase that crystallizes first from the melt.

Melting and Crystallization of Synthetic Slags

Phase Identification

The premelt mixture of oxide powders for the synthetic slags (HA-16, -17, -21, and -22) contained aluminum oxide as mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) plus oxides or carbonates of the other major constituents of Hygas ash. None of the constituent oxides were identified in the x-ray diffraction patterns of the melted slags, indicating that dissolution of the starting materials was complete. Slag HA-16, containing about 9% soda,

Fig. 13. Furnace-Cooled Slag HA-6. (a) Bright field. (b) Polarized light, showing rim of fine-grained Fe_2O_3 surrounding the primary dendrites.

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Fig. 14. Electron Microprobe Displays of Doped Slag Specimen HA-6. (a) Backscattered electron image. (b) Fe $K\alpha$ image. (c) Si $K\alpha$ image. (d) Ca $K\alpha$ image.

consisted of a mixture of glass and one crystalline phase, hematite, after melting at 1200°C for 18 h followed by furnace cooling. The other slag compositions contained about 31% soda. Slag HA-17, melted at 1025°C and furnace cooled, consisted mostly of glass. A few very weak peaks in the x-ray diffraction pattern could not be matched with any compounds detected in the other slags and were not sufficiently resolved to be indexed with confidence. Slag HA-21, melted at 1100°C and furnace cooled, consisted of glass, some $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, and possibly some magnetite. Slag HA-22, melted at 1100°C and water quenched, consisted mostly of glass. These results indicate that increasing the soda content of the basic Hygas slag composition minimizes precipitation of the iron-rich phases and promotes stabilization of a glass structure.

Optical Ceramography

The microstructure of synthetic slag HA-16 (shown in Fig. 15) contained small particles, needles or platelets, and a massive phase, which consisted of an aggregate of smaller crystals all surrounded by a glassy matrix. Slags HA-17, -21, and -22 consisted of glass with no visible evidence of crystalline phases. Since $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and possibly Fe_3O_4 were detected in this sample by x-ray diffraction, we conclude that these phases must be quite small in both size and total quantity. All four synthetic slags contained cracks and/or pores, as evident in Fig. 15, where the cracks are intruded by the ceramographic mounting material.

Electron Microprobe

Electron microprobe results for slag HA-16 are shown in Fig. 16. The crystalline phases (massive crystalline phase and smaller needles in Fig. 15) contain a high concentration of iron. No other elements were detected in this phase, including the dopants Pb, Se, and Te. Therefore, the crystalline phase is evidently relatively pure Fe_2O_3 , as indicated by the x-ray diffraction pattern. The glassy matrix contained Al, Si, K, Ca, and, of course, O. Quantitative chemical analysis

Fig. 15. Furnace-Cooled Synthetic Slag HA-16. The white blocky and needle-like phases are apparently iron oxide. The porous area in the upper left is from gas evolved from the decomposition of carbonate additions.

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Fig. 16. Characteristic X-Ray Spectra for Specimen HA-16. Note that the vertical scales for the two curves are offset slightly to avoid confusion.

indicated Pb, Se, and Te, but their concentrations were below the detection limit for electron microprobe analysis.

Figure 17 shows the characteristic x-ray spectrum for slag HA-22. This spectrum shows the six principal detectable elements in the slag, Na, Al, Si, K, Ca, and Fe. As with HA-16, the concentrations of Pb, Se, and Te are too small to be detected. The spectra for slags HA-17 and -21 were quite similar to that of HA-22.

Devitrification of Glassy Slags

The results of crystallization experiments on Hygas ash and related mixtures showed that even at the relatively low solidification rates used in this study it was not possible to obtain crystalline silicates from these melts. The only crystalline phases to appear during solidification were iron oxides. More importantly the toxic trace elements of interest, such as lead, form low-melting oxides and are apparently rejected into the melt as higher temperature compounds crystallize. Thus, if even a small amount of glass remains, the harmful species would be expected to be segregated in the amorphous phase.

In light of these observations we investigated the devitrification of quenched (glassy) slag. The object was to quench the specimen to produce a glass with the trace elements uniformly distributed. Then if crystalline silicates were subsequently formed by annealing at moderate temperatures, the trace elements might be incorporated into the crystal lattice, and macrosegregation could not occur.

Water-quenched specimens were annealed at 950°C for 2, 24, and 100 h in air. The x-ray diffraction pattern for each was compared with that of the as-quenched material. The diffraction patterns did not indicate the presence of any crystalline silicate phases in the annealed specimens. The observed increase in crystallinity with annealing is only from the precipitation of iron oxide particles. The results are shown in Fig. 18, in which the glass content is seen to decrease with time relative to the crystalline iron oxides Fe_2O_3 and Fe_3O_4 . The relative amounts of glass and crystals are obtained qualitatively by comparing the maximum diffuse intensity at about $25^\circ 2\theta$ (glass) with the

Fig. 17. Characteristic X-Ray Spectrum for Specimen HA-22.

Fig. 18. Relative Glass Content of Quenched Hygas Slags vs Annealing Time at 950°C. The values for slags that were air cooled (AC) and furnace cooled (FC) from the melt are shown for comparison. Water quenching (WQ) results are also shown.

diffracted intensity at about $36^{\circ} 20$ [$2.53 \text{ \AA}$ magnetite (311) peak and $2.51 \text{ \AA}$ hematite (110) peak]. The corresponding values for air-cooled and furnace-cooled samples are shown for comparison. It can be seen that a water-quenched specimen annealed for 2 h at 950°C has about the same glass content as a specimen air cooled from the melt. To approach the crystallinity of a furnace-cooled specimen, the water-quenched slag must be annealed for more than 100 h at 950°C .

The microstructural features of the specimen after a 100-h anneal are shown in Fig. 19. The fine dendritic iron oxides formed around the primary iron oxide particles and also were nucleated strongly at cracks and along the crucible wall. The influence of the cracks is not fully understood, but it could be the result of surface roughness providing nucleating sites. Nucleation was not so strong at the free surface of the specimen, but that surface appears to be smoother than the crack surfaces.

Our results indicate that crystalline silicate phases cannot be developed in this material by annealing at 950°C for reasonable times. However, iron is sufficiently mobile in the glass to form oxide precipitate particles at that temperature.

Soxhlet Extraction

The results of leaching tests using pure water and acidified water ($\text{pH} = 5$) are in Table 6. Since many of the reported Pb, Se, and Te concentrations in the extraction solution are below their detection limits, the results must be considered generally inconclusive. However, a few tentative correlations can be made:

1. Comparison of HA-16 and -17 indicates that the addition of large quantities of soda to the Hygas slag composition increases the release of Pb, Se, and Te. This could result from the modification of the silica network of the glass by the monovalent sodium ions.

2. Comparison of HA-21 and -22 indicates that a slag having the furnace-cooled microstructure is more susceptible to leaching of selenium and tellurium than a water-quenched structure. The possible reasons for this are not well understood at this time.

Fig. 19. Specimen HA-26, Water Quenched and Annealed for 100 h at 950°C, Showing Growth of Iron Oxide Dendrites at cracks (C), primary oxide particles (P), and crucible wall (W). (a) Bright field. (b) Polarized light.

Table 6. Results of Soxhlet Extraction of Hygas and Synthetic Slags in Pure Water and Acidified Water

Sample	Water, ^a pH = 7				Acidified Water, ^a pH = 5			
	Sample Weight (g)	Extraction Concentration, ^b (mg/l)			Sample Weight (g)	Extraction Concentration, ^b (mg/l)		
		Pb	Se	Te		Pb	Se	Te
Blank		<0.01	<0.01	<0.05				
HA-1A	1.00	<0.01	<0.001	<0.05				
HA-3	1.63	<0.1	<0.05	<0.05	0.805	<0.01	<0.001	<0.05
HA-4	1.56	<0.01	<0.001	<0.05	0.954	<0.01	<0.001	<0.05
HA-6	1.04	0.03	<0.001	0.14				
HA-11	1.69	<0.01	<0.001	<0.05	1.080	<0.01	<0.001	<0.05
HA-16	0.99	0.02	0.08	0.33				
EA-17	0.99	0.08	0.24	2.58				
EA-18	0.99	<0.01	<0.03	<0.05	0.072	<0.01	<0.001	<0.05
HA-19	0.99	0.02	<0.001	<0.05	0.056	<0.01	<0.001	<0.05
HA-19 ^c	0.99	<0.01	<0.001	<0.05				
HA-19 ^d	0.99	<0.01	<0.001	<0.05				
HA-20	0.99	<0.01	<0.001	<0.05	0.049	<0.01	<0.001	<0.05
HA-21	0.93	0.09	0.18	3.99				
HA-22	0.94	0.14	0.11	0.63				

^a500 ml; extracted for 24 h except as noted.

^bDetection limits are: Pb, 0.01, Se, 0.001, and Te, 0.05, mg/l.

^cExtracted for 96 h.

^dExtracted for 168 h; a residue in the flask weighed only 10 µg.

3. Specimens HA-17 and -21 were very similar, differing only in their initial melting conditions. It is encouraging to note that the quantities of trace elements extracted from these two samples are fairly comparable.

4. Those specimens that did not release measurable quantities of Pb, Se, and Te in pure water also resisted leaching by an acidic solution. It is possible that stronger acid solutions (representing, say, the limiting case of acid mine drainage, pH = 3-4) would show some leaching.

It appears that the Soxhlet extraction method is appropriate for these materials. However, larger samples would probably yield more useful and sensitive results. It is also possible that the use of highly alkaline solutions (pH = 9-10) would cause a more dramatic release of potentially harmful cations.

A recent study of the leachability of Hygas solids (carbon-rich char) was conducted by Luthy and co-workers.⁹ That study was more concerned with developing a method for assessing the overall leaching characteristics of Hygas solids and did not specifically address the leaching of Pb, Se, and Te. Those investigators found that only B, Ca, Mo, and Na were leached in quantities greater than 0.01% of their initial concentrations in the char when exposed to distilled water, hard water, slightly acidified water, and model acid mine water (pH ~ 3.4) in batch extraction tests. On the other hand, a reducing solution extracted several elements in quantities greater than 1% of their initial concentration in the char. Although the results of Luthy and co-workers cannot be directly compared to our results, both studies suggest that Hygas solids are fairly resistant to leaching by pure water and by slightly acid solutions.

CONCLUSIONS

1. As-received Hygas ash, after removal of the carbonaceous fraction, is composed of quartz, hematite, glass, and a very small amount of magnetite.

2. Melting the ash at 1400°C results in a mixture of silicate liquid and some crystalline iron oxides. This liquid is saturated with iron oxide, and upon cooling considerable amounts of iron oxide are rejected, forming a fine dendritic crystal structure with glass remaining in the interstices. Annealing the melt for several hours at 1400°C causes some of the hematite to transform to magnetite.

3. No crystalline silicates were formed in these melts by slow cooling or by annealing at 950°C after solidification. Annealing the water-quenched (glassy) slags resulted in the precipitation of iron oxide at various nucleating sites. The most dramatic increase in crystal content occurs during the first few hours of annealing.

4. The addition of small amounts of Pb, Se, and Te does not affect the overall course of crystallization of the Hygas slag. These elements are believed to be partitioned into the glassy phase as the high-temperature iron oxide phase crystallizes.

5. The addition of large quantities of Na₂O reduces the liquidus of the slag and generally results in a featureless glassy microstructure, even on relatively slow cooling. Another result is an increase in the leaching rates of Pb, Se, and Te from these materials in neutral and mildly acidic water. The increase in the leachability of these ions from the glass is attributed to a modification of the silica structural network of the glass by the monovalent sodium cations.

RECOMMENDATIONS FOR FUTURE WORK

1. The addition of alkaline earth oxides to wastes such as Hygas, Texaco, and perhaps other gasifier ashes should be studied compositionally in conjunction with sodium and potassium additions to determine if use of the alkaline earth glass network modifiers will decrease the leachability of impurity elements while decreasing the melt working temperatures.

2. Modified crystallized and quenched slag samples should be studied with scanning transmission electron microscopy (STEM) to determine specifically how various toxic elements are partitioned between the crystalline and amorphous phases and how these elements are incorporated into the structure of the crystalline phases.

3. Studies like this one should also be conducted for at least the toxic impurity elements Hg, As, and B.

4. The crystallization of coal conversion waste slags by using controlled rate cooling and selected programmed cooling, including measurements of toxic element extraction from these materials, should be more completely investigated.

ACKNOWLEDGMENTS

The authors would like to thank and acknowledge the following people for their contribution to this work.

W. J. Boegly, Jr., supplied the Hygas ash. O. B. Cavin performed the x-ray diffraction measurements. W. H. Warwick prepared ceramographic samples and took photomicrographs. R. S. Crouse did the electron microprobe analyses. J. W. Geer prepared specimens and assisted in data analysis.

A. E. Pasto and L. D. Hulett, Jr., reviewed the manuscript. The manuscript was edited by B. G. Ashdown and was prepared for publication by Patsy Dickens.

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