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Research on the Characterization and Conditioning of Uranium Mill Tailings

II. Thermal Stabilization of Uranium Mill Tailings: Technical and Economic Evaluation

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by

D. R. Dreesen, E. J. Cokal, E. F. Thode, L. E. Wangen, and J. M. Williams

ABSTRACT

A method of conditioning uranium mill tailings has been devised to greatly reduce radon emanation and contaminant leachability by using high-temperature treatments, i.e., thermal stabilization. The thermally stabilized products appear resistant to weathering as measured by the effects of grinding and water leaching. The technical feasibility of the process has been partially verified in pilot-scale experiments. A conceptual thermal stabilization process has been designed and the economics of the process show that the thermal stabilization of tailings can be cost competitive compared with relocation of tailings during remedial action. The alteration of morphology, structure, and composition during thermal treatment would indicate that this stabilization method may be a long-lasting solution to uranium mill tailings disposal problems.

I. INTRODUCTION

The goal of current uranium mill tailings management technologies is the long-term containment of mobile contaminants. The principal concern is the control of ^{222}Rn releases and water leachable components in tailings. The perceived hazards resulting from such releases prompted the US Environmental Protection Agency (EPA) to propose very stringent standards for the ultimate disposal of tailings at inactive mill sites (US EPA 1980). The proposed standards* would require a radon flux limit of 2 $pCi/m^2/s$ and prohibit the degradation of both surface and ground water.

The most frequently proposed approach to the management of uranium mill tailings relies on barrier systems to contain these hazardous contaminants and prevent their movement into the environment. Los Alamos National Laboratory has investigated a different tailings management approach as part of the technology development program of the US Department of Energy's Uranium Mill Tailings Remedial Action Project (UMTRAP). The physical structure and/or chemical composition of tailings have been altered in this approach to either immobilize contaminants or remove contaminants before disposal. These physicochemical modifications are broadly termed "conditioning" methods.

Our investigations of contaminant immobilization have centered on a process of radically modifying the structure of tailings by sintering at high temperatures, i.e., thermal stabilization. These studies have included (1) the initial laboratory proof-of-concept experiments to characterize the reduction in contaminant release potential, the mineralogical changes resulting from thermal stabilization, and the resistance of these products to physical and chemical degradation; (2) the preliminary engineering of a conceptual process and an analysis of the economics; (3) a pilot-scale thermal stabilization study to better verify the technical feasibility of this process; and (4) a final engineering and economic evaluation based on the pilot-scale experimental results.

*Final standards were published in Federal Register 48 FR 590, January 5, 1983.

II. PROOF-OF-CONCEPT LABORATORY EXPERIMENTS

A. Radon Emanation Reduction

To perform conditioning experiments on a modest number of samples, we composited individual samples in an effort to represent the range in composition. The composites were prepared from the individual samples [locations shown in Figs. A-1, A-2, and A-3 of Vol. I (Dreesen et al. 1983)] and include

Shiprock

SHIP Sands — composite of high SiO_2 content samples (other elements low); 77% sand sized (>50 μm).

SHIP Fines — composite of low SiO_2 and high major/minor trace elements; 27% sand sized.

Salt Lake City

SLC 1AB — high SiO_2; low Fe, Mn, As, Se, V; 50% sand sized.

SLC 4AB — high Al, As, Se; low SiO_2; 34% sand sized.

SLC 5AB — high Ca, Fe, Cl, Cr, Mn, V; low SiO_2; 64% sand sized.

Durango

DGO LP — all large pile samples, fairly homogeneous; 55% sand sized.

DGO SP Sands — high SiO_2; low Al, Ca, Fe, Na; 84% sand sized.

DGO SP Fines — high Al, As, Ca, Fe, Na, V; low SiO_2; 31% sand sized.

Ambrosia Lake

AML Fines — high Al, K, Na, Se, Mo; 10% sand sized.

In a preliminary series of heat treatments, ^{222}Rn emanation reduction was determined as a function of sintering temperatures ranging from 750 to 1150°C. Significant radon emanation reduction (>95%) was not obtained until temperatures exceeded 1050°C (see Table A-I in Appendix A). Because we hoped to achieve a 200-fold reduction, 1200°C was selected as a temperature that (1) could produce such a reduction with some tailings, (2) might be technologically feasible on a large scale, (3) would not subject fire clay crucibles to excessive temperatures, and (4) would permit tailings evaluations under constant conditions. Procedures for this proof-of-concept experiment are described in Appendix A.1.

The amount of material lost during heating was appreciable for some samples [up to 25% (see Table I)]. It is assumed that the material lost would include waters of hydration and volatiles from the decomposition of carbonate and/or sulfate salts.

The reduction in emanation for tailings composites is summarized in Table I for oxidizing conditions (i.e., fire clay crucibles) and reducing conditions (i.e., graphite crucibles). Under oxidizing conditions, the emanating ^{226}Ra of sintered tailings was reduced by factors of 37 to 1400, with emanating ^{226}Ra ranging from 0.27 to 1.58 pCi/g. Under reducing conditions, the emanating ^{226}Ra ranged from 0.12 to 1.72 pCi/g (i.e., reductions of 22- to 1100-fold). Because replicate emanating ^{226}Ra measurements on the same sample were within 10%, the differences between samples appear to be real.

Reducing conditions favored lower emanation, particularly for the iron-rich SLC 5AB and the DGO SP Fines tailings. (See Dreesen et al., Vol. I, 1983, for description of untreated tailings.) In contrast, oxidizing conditions caused lower radon emanation for SHIP and DGO SP Sands, as well as AML Fines.

B. Mineralogy of Thermally Stabilized Tailings

By examining the emanation results in relation to the mineralogy, we found that those samples exhibiting the greatest emanation reduction were generally those with lesser quartz content (i.e., fines) and which formed glassy slags. The high-quartz tailings (>60%) formed masses of slightly fused sands, which had emanation reduction factors of less than 250. The iron-rich SLC 5AB tailings exhibited sintering behavior more characteristic of tailings sands under oxidizing conditions but formed a glassy slag under reducing conditions. This variable behavior may result from the formation of different high-temperature mineral products under different O_2 conditions.

The predominant plagioclase and nonaluminum silicate minerals present in DGO LP and DGO SP Fines

TABLE I

RADON EMANATION FROM THERMALLY STABILIZED TAILINGS

		Untreated Tailings			Thermal Stabilization at 1200°C			
					Oxidizing Conditions		Reducing Conditions	
Site	Composite	Emanating ^{226}Ra (pCi/g)	SiO_2 %	Mass[a] Loss on Heating (%)	Emanating ^{226}Ra (pCi/g)	Reduction[b] Factor	Emanating ^{226}Ra (pCi/g)	Reduction Factor
SHIP	Sands	39	90	5	1.03	37	1.72	22
SHIP	Fines	214	53	25	0.62	350	0.48	450
SLC	1AB	136	75	12	1.33	100	0.64	210
SLC	4AB	125	61	16	0.44	280	0.44	280
SLC	5AB	63	43	4	0.38	170	0.12	530
DGO	LP	212	67	2	0.27	790	0.32	660
DGO	SP Fines	473	57	7	1.58	300	0.43	1100
DGO	SP Sands	140	87	2	0.75	190	1.71	82
AML	Fines	546	–	9	0.39	1400	0.55	990

[a]Under oxidizing conditions 1200°C.
[b]Reduction factor = Emanating ^{226}Ra (untreated tailings)/Emanating ^{226}Ra (thermally stabilized tailings).

appear to have fairly low melting points or undergo slag-forming mineral reactions at 1200°C. The AML Fines have considerable clay and albite (mp 1100°C) content along with $NaHCO_3/Na_2CO_3$ (a fluxing agent) from the mill process (Merritt 1971), which could favor the formation of glassy slag. Photographs of these thermally stabilized tailings are shown in Figs. A-1 through A-15 in Appendix A.

The above observations and inferences concerning the mineralogy of thermally stabilized tailings coincide well with x-ray diffraction results. X-ray diffraction patterns are illustrated in Fig. 1 for untreated Shiprock Fines, as well as samples heated to 1200 and 1400°C. As is readily apparent, the structure of the tailings has been greatly modified by sintering. The 1200°C material shows the disappearance of peaks corresponding to gypsum, clays, illite, kaolinite; the decrease in the peak heights for quartz; and the appearance of anhydrite. In addition, the amorphous region (the baseline corresponding to 2θ values from 15 to 35) has substantially increased in area. The complete amorphous character of the 1400°C sample is apparent in Fig. 1 with the disappearance of all peaks including that for quartz.

The reduction in quartz content and increase in amorphous material for the tailings composites heated to 1200°C (in fire clay crucibles) are reported in Table II. Decreases in quartz content ranged from 0 to 35%; increases in amorphous material ranged from 5 to 65%. The amount of amorphous character was determined as a relative percentage based on the area in the "amorphous region" (2θ ranges from about 15 to 35) being 100% for the SHIP Fines sample heated to 1400°C (see Fig. 1). This sample showed no discernable mineral content and was thus assumed to be totally amorphous. The origin of this amorphous material was principally quartz for some tailings (SHIP Fines, AML Fines, and DGO SP Sands), but mainly plagioclase-type minerals for DGO LP and DGO SP Fines. Another group of minerals also disappeared from the diffraction patterns of the 1200°C samples: gypsum, illite, clays, albites, kaolinite, apatite, barite, and calcite. Some anhydrite ($CaSO_4$) is present in the thermally stabilized tailings (see Fig. 1) and is most likely produced from gypsum ($CaSO_4 \cdot 2H_2O$). The decreased radon emanation for SHIP Fines and SLC 1AB (both having high initial gypsum contents) under reducing conditions may result from the decomposition of gypsum to CaO, which should act as a fluxing agent to promote vitrification of these tailings. In addition, new silicates (e.g., cristobalite), Na, Ca, or Fe silicates, and Na, Ca, or Fe aluminosilicates are apparently present. Thus, the exact mineral transformations caused by sintering at 1200°C

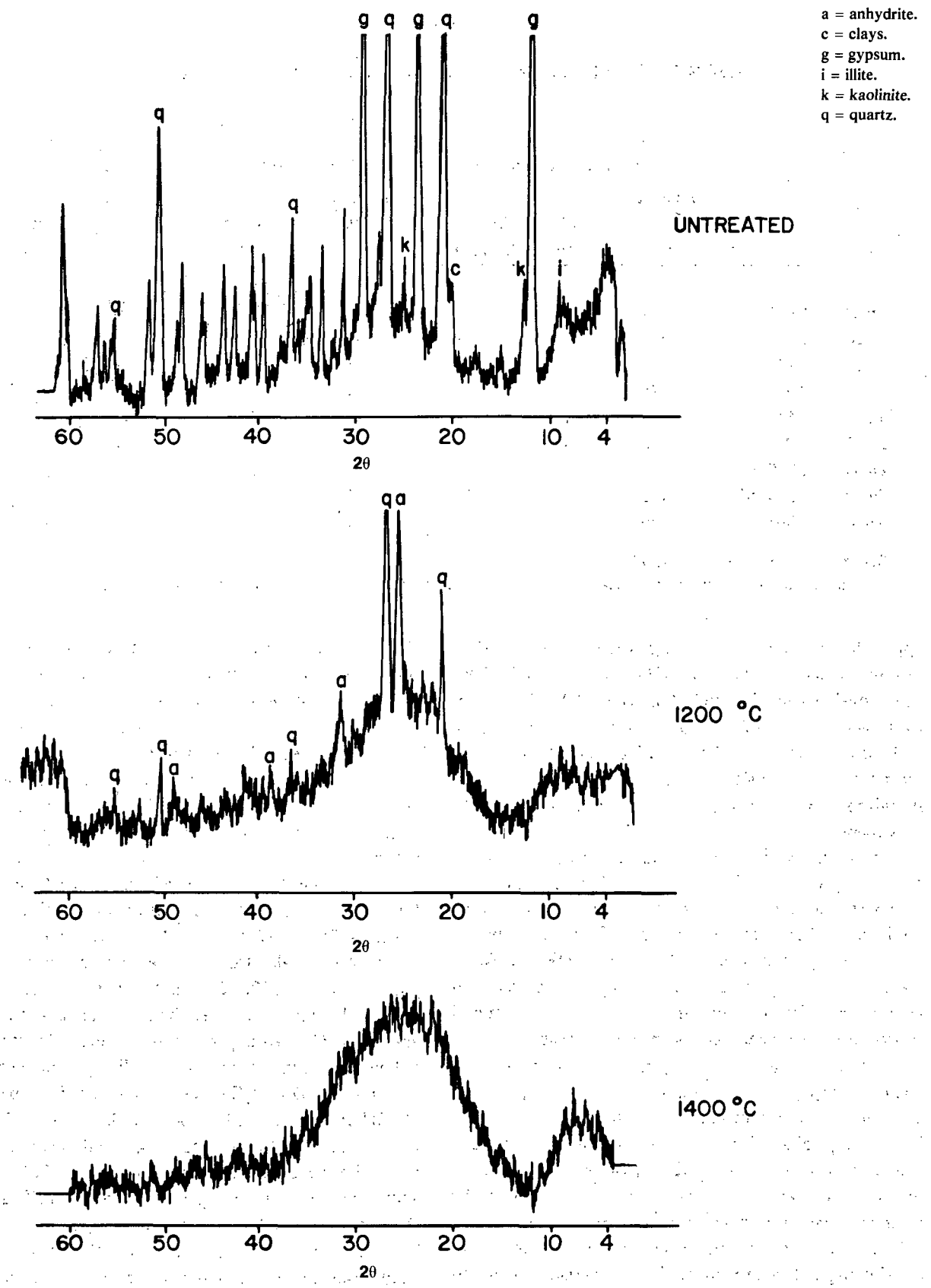

Fig. 1. X-ray diffraction patterns for SHIP Fines, untreated or sintered at 1200 and 1400°C.

TABLE II

CHANGES IN QUARTZ AND AMORPHOUS MATERIAL RESULTING FROM THERMAL STABILIZATION

		Percentage Quartz		Amorphous Material	
Site	Composite	Untreated (%)	1200°C Treatment (%)	Untreated (%)	1200°C Treatment (%)
SHIP	Sands	90	80	20	25
SHIP	Fines	25	10 (0)[a]	20	40 (100)[a]
SLC	1AB	70	45	20	60
SLC	4AB	35	25	35	60
SLC	5AB	35	40	5	20
DGO	LP	45	25	10	75
DGO	SP Fines	15	15	15	80
DGO	SP Sands	90	65	5	25
AML	Fines	45	10	25	75

[a]Heated to 1400°C.

are not easily delineated. The formation of amorphous material and the new minerals produced may cause reductions in emanation power because of the incorporation of ^{226}Ra into these components and reduced surface area.

C. Aqueous Leachability of Contaminants in Thermally Stabilized Tailings

Another measure of the efficacy of thermal stabilization as a remedial action technology is the reduction in contaminant leachability. Batch leaching tests (25 g tailings/125 mℓ H_2O) were performed on both untreated and thermally conditioned (1200°C) tailings. The concentrations of hazardous constituents and major ions in these leachates were determined as described in Appendix A.2 and are presented in Tables A-IV and A-V. Concentrations for untreated tailings leachates exceed the proposed EPA water contamination standards for many of the elements, including As, Cd, Mo, Pb, Se, U, and ^{226}Ra. The thermal stabilization treatment reduces the leachability of most of these contaminants, including uranium, which exhibits a very large decrease. However, Ba, Mo, and ^{226}Ra are apparently more leachable in some of the thermally stabilized acid tailings (SHIP and SLC). After thermal treatment, barium leachability increases by factors of 5 to 10 for acid tailings; in comparison, ^{226}Ra exhibits minor increases or substantial decreases in leachability for these materials. Thus, the aqueous leachability of Ba is not analogous to Ra in these leaching experiments.

When considering the elements not included in the proposed water contamination standards (see Table A-V), the most noticeable change as a result of thermal stabilization for the alkaline tailings is a pronounced decrease in sodium leachability, probably resulting from the incorporation of sodium into silicates or aluminosilicates. The substantial amount of leachable iron in the untreated alkaline tailings suggests the presence of Fe(II). Thermal treatment could oxidize Fe(II) or cause its incorporation into silicates, making it immobile. Vanadium also exhibits a substantial decrease in leachability; the formation of water insoluble calcium vanadates or uranates may occur during thermal treatment as it does in the salt roasting of uranium ores (Merritt 1971). The untreated acid tailings leachates are dominated by Ca^{+2} and SO_4^{-2}. However, when heated to glass-forming temperatures (>1200°C), anhydrite apparently decomposes to CaO and sulfur oxides. Acid-mobile constituents, such as Fe, V, Al, Cd, Pb, Zn, Mn, and Ni, are virtually immobilized in the thermally stabilized tailings (TST) as a result of the neutral or alkaline character of these leachates or the incorporation of these elements into insoluble minerals or glasses. Alkaline mobile elements (e.g., Mo and Se) are still

readily leached from the tailings (thermally treated in the laboratory), which had neutral to alkaline leachates.

Thermal stabilization can substantially reduce the mobility of a number of contaminants, including those listed in the proposed EPA regulations. The leachability of a few elements appears unaffected by sintering or may actually increase. A basic question in evaluating leachability is to determine whether these problem contaminants are leached rapidly from the thermally stabilized tailings or are a persistent, long-term pollution source. Therefore, even if high initial leachate concentrations are encountered, over the long term, conditioned tailings may release only a small fraction of contaminants that are leachable from untreated tailings.

D. Experimental Assessment of the Long-Term Stability of Thermally Stabilized Tailings

1. Changes in Emanating Power

A preliminary assessment of the effects of weathering TST was performed to evaluate whether physical degradation and leaching would increase radon emanation. Physical degradation was simulated by pulverizing the crushed (<6 mm) sintered tailings to <0.85 mm. Emanating ^{226}Ra was measured on (a) untreated tailings, (b) crushed sintered tailings (<6 mm), (c) pulverized sintered tailings (<0.85 mm), and (d) leached (with deionized water) and pulverized sintered tailings (<0.85 mm).

Reduction factors for crushed (<6 mm) and "weathered" (pulverized and leached) sintered tailings, compared with emanation power of untreated tailings, are presented in Table III. Sintered tailings crushed to <6 mm have radon emanation reduced by factors of 100 to 2300 vs untreated tailings. The levels of emanating ^{226}Ra in the weathered thermally stabilized tailings (pulverized and leached) range from 0.3 to 11 pCi/g, corresponding to reduction factors of 20 to 300 (Table III, column U/PL).

The effects of pulverizing the sintered tailings on radon emanation are illustrated in the pulverized/sintered (P/S) column of Table III. The tailings sands, which retained a sandy texture after thermal stabilization, show P/S ratios of 1.2 to 1.6. Thus, the pulverizing had a relatively small effect on the sandy or slightly fused sands produced by thermal conditioning. The tailings fines that formed slags or the glass (SHIP Fines, 1400°C) showed a greater effect from pulverization; P/S ratios ranged from 2.3 to 4.3. Pulverization obviously causes a greater alteration in the structure and surface area of slags than of tailings that have not undergone melting and have retained a sandy texture. Thus, if increases in radon emanation power are used as a measure of the extent of weathering, slags from thermal

TABLE III

EMANATION REDUCTION FACTORS FOR THERMALLY STABILIZED TAILINGS (1200°C); RATIOS OF EMANATING POWER SHOWING THE EFFECTS OF GRINDING AND LEACHING

Initial Texture[a]	Initial Gypsum[b]	S[c]	U/S	U/PL	P/S	PL/P	PL/S
Sands	15 %	1.2	100	34	1.3	2.3	3.0
	≤7 %	0.2 – 0.4	100 – 450	51 – 240	1.2 – 1.6	1.2 – 1.3	1.4 – 2.0
Fines	35 %	0.9	230	20	2.5	4.7	11.6
		[0.2][d]	[1200]	[170]	[4.3]	[1.7]	[7.3]
	≤7 %	0.2 – 0.5	370 – 2300	95 – 300	2.3 – 4.3	1.7 – 1.8	3.9 – 7.5

[a]Tailings with >50% sand-sized particles = sands.
[b]Gypsum content as determined by x-ray diffractometry.
[c]Emanating power (pCi/g) of U = Untreated tailings;
S = Sintered 1200°C, crushed < 6 mm;
P = Sintered 1200°C, pulverized <0.85 mm; and
PL = Sintered 1200°C, pulverized <0.85 mm, leached.
[d][] indicates vitrified material, i.e., formed at 1400°C.

stabilization will undergo greater alteration by a given amount of physical degradation than will granular materials.

The effect of leaching on radon emanation is illustrated by the pulverized and leached/pulverized (PL/P) ratios of Table III. Two groups can be discerned from these results: a low initial gypsum (<7%) *group* in which sands have PL/P ratios of 1.2 to 1.3 and fines (slags) have ratios of 1.7 to 1.8; a high initial gypsum (15 to 35%) *group* in which sands have a ratio of 2.3 and fines have a ratio of 4.7. Tailings with high initial gypsum contents contain appreciable anhydrite ($CaSO_4$) after sintering in oxidizing conditions. The initial presence of large amounts of gypsum (dehydrated to anhydrite by heating) may cause structural damage within the sintered material as a result of the rehydration of this mineral. Some evidence of this mechanism was seen in the glass produced from high gypsum fines that had been heated sufficiently to completely decompose anhydrite as shown by the very small amounts of leachable Ca^{+2} and SO_4^{-2} and the absence of any anhydrite peaks in the x-ray diffraction patterns. The increase in emanation for this glass because of leaching, i.e., the PL/P ratio, is 1.7 and is similar to that for low-gypsum slags. Thermally conditioned (1200°C) tailings having high gypsum levels show the greatest increase in emanation because of leaching and contain the most leachable Ca^{+2} and SO_4^{-2} of all the sintered tailings.

The combined effects of both pulverization and leaching are given as the pulverized and leached/-sintered (PL/S) ratios in Table III and can be used as a measure of weathering potential. Low weathering potential, PL/S ≤ 2 (i.e., greater stability), is seen for low gypsum sands. Moderate weathering potential, PL/S = 3 to 7.5, is found for high–gypsum sands, low–gypsum fines, and the glass (high initial gypsum, low final anhydrite). High weathering potential, PL/S = 11.6, is found only for the high-gypsum tailings fines. However, it must be remembered that radon emanation of weathered TST is still reduced by 95 to 99.7% compared with untreated tailings.

2. Changes in Leachable Constituents

Untreated and thermally stabilized tailings were batch leached three times in succession to assess the dissolution of major constituents (e.g., gypsum/anhydrite) and contaminants resulting from the equivalent of approximately 30 pore volumes of water (assuming 50% pore volume) contacting these materials.

For untreated acid tailings, the pH rose from 1/2 to 1 unit after three leaches. Calcium and sulfate continued to be highly leachable, with concentrations still controlled by the solubility of gypsum. The concentrations of Mg, Pb, and U dropped substantially for the acid tailings [excluding the SLC 5AB (ferrophos) material, pH = 8.1]. In addition, V and Mo levels decreased rapidly in the three successive leaches of the acid tailings fines.

The thermally treated acid tailings leachates (SLC and SHIP) have neutral to alkaline pH values and exhibit reduced Ca^{+2} and SO_4^{-2} concentrations in the successive leaches, except for the SHIP Fines. As seen in Table IV, up to 18 times more SO_4^{-2} is leachable from untreated acid tailings than from TST. Molybdenum leachability from TST decreased rapidly in most cases, although more Mo was leached from most TST than from untreated tailings. The amounts of Mg, V, and U leachable from the conditioned tailings were small compared with the amounts extracted from untreated tailings (see Table IV). With repeated leaching, the SHIP Fines, high in anhydrite after thermal treatment, exhibited no decreases for several leachable constituents.

The alkaline tailings generally show a pattern of much more leachable Ca, SO_4^{-2}, Mg, V, and U in the untreated tailings than in the thermally stabilized material. The untreated AML Fines contain little leachable Ca, SO_4^{-2}, or Mg, but substantial SiO_2; thermal treatment causes a substantial decrease in SiO_2 concentrations while moderating pH near neutrality.

The results summarized in Table IV substantiate the conclusion that Mo and Ba are the only elements identified that exhibit increased leachability from thermally conditioned tailings. However, the Ba levels are initially below the EPA standard, and the Mo in almost all materials drops below the standard after the first leach of TST (approximately 10 pore volumes).

E. Radon Emanation and Mineralogy as Influenced by Sintering Temperature

The complex relationship between the reduction in emanation power and changes in mineralogy caused by sintering prompted an experiment to investigate these changes as a function of sintering temperature. Sands and fines from the Shiprock and Durango tailings piles were sintered at temperatures ranging from 500 to 1200°C. The emanating ^{226}Ra for both Shiprock and Durango tailings, as well as major mineral forms present in the Shiprock samples, was determined.

TABLE IV

RATIO OF TOTAL AMOUNT OF ELEMENT EXTRACTED FROM UNTREATED TAILINGS DIVIDED BY TOTAL EXTRACTED FROM THERMALLY STABILIZED TAILINGS

(3 successive batch leaches)

Site	Material	Ratio Final pH[a]	Ba	Ca	Mg	SO_4^{-2}	SiO_2	Pb	Mo	V	U
SHIP	Sands	4.5/7.8	0.1	14	24	18	2	>8	<0.2	0.3	45
SHIP	Fines	3.8/6.7	0.3	0.9	53	1.0	7	>14	<0.2	>23	190
SLC	1AB (Sands)	3.7/7.5	0.1	3	18	3	3	>4	<0.1	–	590
SLC	4AB (Fines)	3.4/6.9	0.3	9	71	14	5	>60	1.6	>54	330
SLC	5AB (Ferrophos)	8.1/7.8	~1	35	34	165	5	–[b]	1.8	91	4
DGO	LP (Fines)	9.3/7.9	0.8	6	6	2	0.9	–	–	12	58
DGO	SP Sands	9.1/7.2	3	5	13	48	4	–	0.1	13	64
DGO	SP Fines	8.4/7.6	0.1	7	10	10	6	–	4	25	170
AML	Fines	9.3/7.4	12	0.6	0.7	1.5	20	>5	>9	>9	230

[a]pH of third leach of untreated tailings/pH of third leach of TST.
[b]Concentration less than detection limit.

The weight loss caused by heating ranged from 11% at 500°C to 24% at 1200°C for SHIP Fines. Corresponding losses for SHIP Sands were 2 to 5%, DGO SP Fines 3 to 6%, and DGO SP Sands 1 to 2%.

The percent reduction in emanating ^{226}Ra of these tailings as a function of sintering temperature is shown in Fig. 2. Table V summarizes these data in terms of percent reduction in emanating ^{226}Ra. For SHIP Fines (emanating ^{226}Ra 214 pCi/g), most of the reduction occurred between 700 and 1000°C (134 to 8.3 pCi/g); however, sufficient reduction (i.e., to 1-2 pCi/g) required temperatures greater than 1100°C for both SHIP Fines and Sands. As seen in Fig. 2 and Table V, the Durango tailings show much greater emanation reduction (up to 800°C) than the Shiprock samples. From 800 to 1000°C, the reduction in emanating ^{226}Ra was not as great; however, between 1000 and 1200°C, the emanating ^{226}Ra decreased substantially. As with the Shiprock samples, the Durango tailings required sintering temperatures of 1100°C or greater to reduce the emanation power to 1 to 2 pCi/g.

These results illustrate that to achieve substantial reduction (i.e., >95%) in emanating power requires treatment at temperatures of 1100 to 1200°C. This temperature range corresponds with the thermal treatments necessary to produce large increases in amorphous material and large reductions in surface area. Such reductions in surface area were shown by measuring nitrogen BET surface area for both thermally stabilized and untreated SLC tailings (–20 mesh, <0.8 mm); the surface area of untreated tailings was 15 to 17 m^2/g, and tailings sintered at 1200°C (which were slightly fused) had surface areas of less than 0.1 m^2/g. As shown in Fig. 3, treatment temperatures greater than 900°C are required to produce significant reductions in surface area. Increased surface area at 500°C may result from mineral structure alterations caused by dehydration. However, radon emanation was reduced by treatment at 500°C (see Fig. 2) for Durango and Shiprock tailings. Thus, it appears that substantial reductions in emanating power result from greatly reduced surface area, mineral transformation and lattice rearrangements, and increased vitreous (amorphous) material sealing or joining mineral grains.

The mineral transformations occurring over this range of temperatures were determined by x-ray diffractometry for SHIP Fines and Sands. The inferred changes in the mineralogy of SHIP Fines are as follows:

(1) gypsum disappears before 500°C (i.e., $CaSO_4 \cdot 2H_2O \rightarrow CaSO_4$ at 163°C); anhydrite is found at 500°C and above but appears to start decreasing at 1000°C and is reduced by ~75% at 1200°C;

(2) quartz does not change substantially until 1200°C, where about 60% is transformed, perhaps to cristobalite (synthetic SiO_2) or to calcium silicates;

(3) clay minerals, including illite, disappear at 900°C;

(4) kaolinite seems to disappear by 500° C;

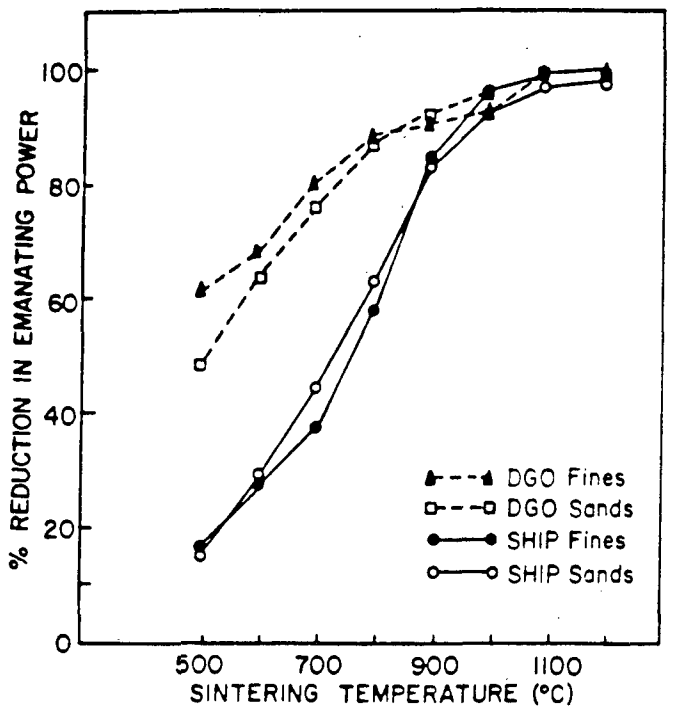

Fig. 2. Percent reduction in ^{222}Rn emanating power as a function of the sintering temperatures used in thermal stabilization.

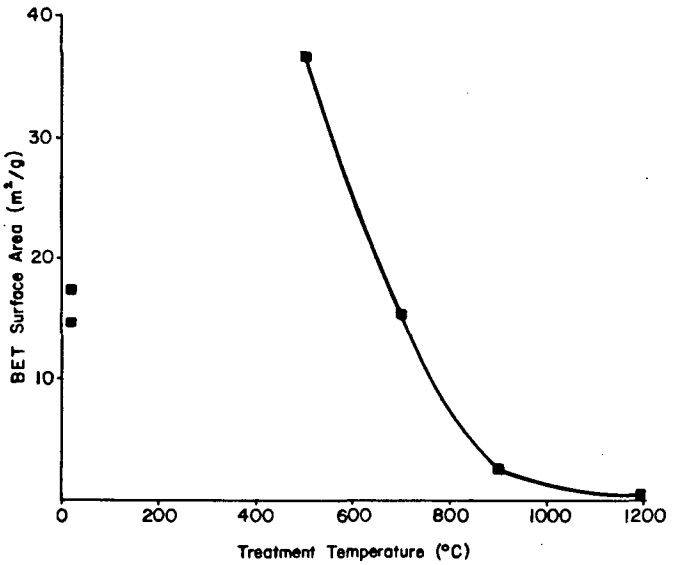

Fig. 3. BET surface area of SLC 4AB (Salt Lake City Fines) tailings as a function of treatment temperature.

TABLE V

PERCENT REDUCTION IN EMANATING ^{226}Ra AT TEMPERATURES FROM 500 TO 1200°C[a]

Sintering Temperature (°C)	SHIP Sands[b] (%)	SHIP Fines[b] (%)	DGO SP Sands[b] (%)	DGO SP Fines[b] (%)
500	15	16	48	61
600	29	27	64	68
700	44	37	76	80
800	63	58	87	88
900	83	84	92	91
1000	92	96.1	95.5	92
1100	96.4	98.8	99.0	99.8
1200	97.7	99.2	99.5	99.8

[a](1.0 – treated tailings/untreated tailings) × 100%.
[b]Original emanating ^{226}Ra.
SHIP Sands = 39 pCi/g.
SHIP Fines = 214 pCi/g.
DGO SP Sands = 140 pCi/g.
DGO SP Fines = 473 pCi/g.

(5) new minerals (possibly plagioclase-type) are forming at about 900°C when the clay minerals and albite are disappearing;

(6) the amorphous content seems to have increased at 1100°C to about twice the original content.

The gypsum and anhydrite response for SHIP Sands parallels that for SHIP Fines. Quartz seems somewhat reduced (~10%) only at 1200°C. Calcium silicates and cristobalite appear to be the high-temperature mineral products.

The reduction in emanation power between 700 and 1000°C for SHIP Fines seems to correspond with the destruction of clays; however, to reach emanating ^{226}Ra levels of 1 pCi/g apparently requires production of increased amorphous character. In addition, the apparent formation of calcium silicates and/or calcium aluminosilicates at temperatures of 900°C or greater could also immobilize radium in structures that limit the escape of radon gas. The more gradual decrease in emanating power for SHIP Sands does not seem to directly relate to changes in mineralogy.

III. ENGINEERING AND ECONOMIC ANALYSIS OF THERMAL STABILIZATION

If conditioning is to be a viable remedial action alternative to some purely physical (barrier) method such

as liners or covers, or is to be used in conjunction with a physical method, it must meet two conditions. First, it must be amenable to application of existing technology on a large scale with a minimal time needed to adapt the technology. Second, the projected remedial action costs involved must be reasonably comparable with those of "equally effective" alternatives. Details of this technoeconomic analysis can be found in Appendix B.

Costs of any remedial action strategy cannot be generalized across different tailings sites. Local factors make the cost of each alternative differ greatly between sites. Such site-specific factors mean that the economically desirable alternative at one site may be unacceptable at another.

The preliminary conceptual design of the process to perform the thermal treatment was developed around the application of a used coal-fired rotary cement kiln. The kiln would be moved to the tailings site, and appropriate feed apparatus and particulate and gaseous emissions control equipment would be installed. The sintered product or slag would be piled on site and covered with a 0.5-m layer of earth to attenuate the gamma field and to aid revegetation.

Cost estimates have been calculated on the basis of the coal-fired rotary kiln concept for remedial action at Shiprock, Salt Lake City, and the residues at Canonsburg, Pennsylvania (Thode and Dreesen 1981). The estimated cost for performing thermal stabilization at Salt Lake City is $32.00/t (t = metric ton or 1000 kg) for a 450 t/d facility; the overall cost would be $76 million. A comparison of a 450 t/d and a 900 t/d facility was made for the Shiprock site; the overall costs were determined to be equivalent at $17.50/t or a total of $27 million. The lower cost at Shiprock results from lower coal, electricity, and manpower costs than at Salt Lake City. The cost of thermal stabilization at Shiprock is approximately the same as moving the pile a moderate distance (~10 km) but appreciably more than covering the existing pile in place. The estimated cost of thermal stabilization of Canonsburg tailings is significantly higher ($45.50/t) because of the large capital expense involved in treating a relatively small amount of tailings (~180 000 t). Thus, the site specifics are very important in determining the costs of thermal stabilization.

Because the cost of coal is a substantial portion (up to 20%) of the overall cost, alternative fuel sources have been evaluated. In those cases where the tailings pile is near a large population center (e.g., Salt Lake City), municipal refuse or dewatered sewage sludge could be used as alternative fuels. Codisposal offers the economic advantage of an investment in capital equipment that can be used for the incineration of municipal wastes long after the thermal treatment of tailings is completed; the energy output in the form of steam, steam-generated electricity, or low-Btu gas could be diverted to off-site uses at the completion of thermal stabilization. Initial engineering evaluation of existing technologies indicates that it is not currently possible to achieve a one-stage simultaneous waste-incineration/tailings-conditioning process. The prospects of a two-stage process have been evaluated. The first stage would pyrolyze municipal waste into low-Btu gas, which would fire the second-stage kiln or furnace where the tailings would be thermally treated. For details of this evaluation see Appendix B.

IV. PILOT-SCALE THERMAL STABILIZATION EXPERIMENT

The success of our initial thermal stabilization experiments in reducing the radon emanation and contaminant leachability of uranium mill tailings prompted a larger scale test of this process to better simulate the sintered product from a full-scale operation. Because of the great material input required for a continuous thermal process (e.g., rotary cement kiln), we decided to conduct these pilot-scale tests in a rotary batch furnace. Such a device was available at the U.S. Smelting Furnace Company, Belleville, Illinois; Los Alamos personnel made arrangements to conduct one week of thermal stabilization tests using a 1-ft^3 (working capacity) rotary furnace.

Thermal stabilization tests were performed on Salt Lake City tailings because (1) this site was one of only a few where thermal stabilization might be economically competitive with other remedial actions; (2) this site would be one of the first sites where remedial action would be performed; and (3) there was a slight chance that thermal stabilization could be combined with a municipal refuse incinerator planned for this site.

A. Test Procedures and Results

The extensive efforts in preparing tailings material to be used in these pilot-scale tests are described in Vol. I (Dreesen et al., Vol. I, 1983). Several different materials were prepared from the Salt Lake City tailings:

- AVG — +1/8- to 1/2-in. agglomerates prepared from homogenized tailings blended from representative amounts of each of the various sections of the Salt Lake City tailings pile;

- LARGE — +1/2-in. agglomerates with same composition as AVG;

- COAL — +1/8- to 1/2-in. agglomerates prepared from the homogenized tailings with powdered (–20 mesh) subbituminous Utah coal blended in to attain a 10% coal material;

- MIX — +1/4-in. agglomerates where each section of the tailings pile is proportionally represented; however, each individual agglomerate represents tailings from only one section, i.e., the agglomerates are heterogeneous; and,

- NaOH — +1/8- to 1/2-in. agglomerates prepared from homogenized tailings that had been wetted with sufficient NaOH to achieve an ~5% NaOH content (3% additional Na).

The AVG material was most representative of the average composition of the SLC tailings. The COAL material was tested to determine if a reducing atmosphere might promote the decomposition of SO_4 (primarily $CaSO_4$) and produce CaO, which would act as a fluxing agent to promote vitrification. The MIX material would show how heterogeneity in the input would affect the efficacy of thermal stabilization. The NaOH treatment was an attempt at assuring a more vitrified material because of the fluxing action of NaOH.

Preliminary heating tests in a box furnace indicated that temperatures of 1100 to 1150°C produced well-sintered agglomerates with negligible deformation. Thus, we had an estimate of the temperatures that should be used in the pilot-scale rotary furnace tests. Because the temperatures measured in the pilot-scale tests are furnace wall temperatures determined with an optical pyrometer, the agglomerates actually intermittently experienced higher temperatures when exposed to the natural gas flame. However, the mean agglomerate temperature at the end of a test run probably approximated the wall temperatures. Treatment temperatures of 1000 to 1100°C were tested for sintering agglomerates. Several test runs were carried out at very high temperatures (1525°C) to produce glasses from the tailings.

The time necessary to bring small charges (i.e., 4.5 kg) to temperature ranged from 3 to 6 min—this parameter will be referred to as the heatup time. The residence time at temperature or treatment time ranged from 2.5 to 60 min for various test runs.

Table C-I in Appendix C presents the test run number, the date and time the test charge was loaded, the sample input amount and type, the treatment temperature, the heatup time, the treatment time, the type of quenching employed, and the furnace operation mode. Notes made during the test runs are presented in Table C-II in Appendix C and describe observations regarding product appearance, flame operation, off-gassing, and quenching. Photographs of the various input and TST materials are shown in Appendix Figs. C-1 through C-8. Figures C-9 through C-11 are photomicrographs of thin-sectioned, thermally stabilized agglomerates, which were vacuum-impregnated with epoxy before sectioning and polishing.

The loss of weight resulting from thermal stabilization was based on the enrichment in nonvolatile elements (Na, Al, V, Mn, Ca, and U) following treatment. These results are reported in Table C-III and show that the elemental content of the AVG material was enriched by a factor (concentration ratio) of 1.143 or a corresponding weight loss of 12.5%. No significant increase in the concentration ratio (i.e., weight loss) was apparent when the treatment temperature increased from 1000 to 1100°C. The volatiles probably resulted from the vaporization of water, carbonates, and perhaps sulfates and chlorides. The weight loss from the COAL material was 18.1% or a concentration ratio of 1.221. A small, but not significant, increase in weight loss was noted as the temperature increased. The combustion of coal causes the additional weight loss from these tailings.

The loss of volatile minor and trace elements during thermal treatment was also determined by neutron activation analysis (NAA) of input and output material. The results are summarized in Table C-IV to show the percentage of total element lost and the microgram of element lost per gram of tailings input, i.e., corrected for weight loss. Substantial amounts of Cl and As are lost during the treatment of both AVG and COAL materials (50 to 60% of the Cl and 60 to 80% of the As). Substantially more Sb was lost from COAL materials, possibly because the more reduced conditions promoted the formation of volatile hydrides or hydrocarbons. About 40 to 60% of Se was lost from the COAL input. For these four elements, appreciably lower losses were found at the 1000°C temperature.

Determinations of radionuclide content on both input and output materials provided a means of assessing volatility of ^{210}Pb, ^{227}Ac, ^{234}Th, ^{230}Th, and ^{226}Ra (see Table C-V). Because of the large analytical uncertainties associated with low-energy ($\leq$100 keV) gamma counting, we judge that only consistent large differences in content are significant. Thus, ^{210}Pb appears to be quite volatile, with about 80% lost during thermal stabilization; for the COAL materials, there is some evidence that increasing losses occur at higher temperatures. An apparent loss of 30 to 40% of the ^{227}Ac was found. For the other radionuclides, $^{234}Th(^{238}U)$, ^{230}Th, and ^{226}Ra, losses are not generally appreciable so we surmise little or no volatility for these elements.

The mineralogy of both the untreated input, as well as the thermally stabilized tailings, was determined by powder x-ray diffraction methods. The untreated materials contained 40 to 50% quartz, with substantial amounts of feldspars, chloroapatite, hematite, and some gypsum. The quartz contents were moderately reduced by thermal treatment by about 10%. The feldspars were reduced by 20 to 40% for the AVG material and by 50 to 60% for the COAL input. Hematite and gypsum were not detected in the treated samples. Chloroapatite was not detected for the products of test runs #15, 27C, 28C, and 29C. However, the chloroapatite peaks were reduced by two-thirds for samples #13 and #14 and one-half to two-thirds in samples #28B and #29B. Thus, chloroapatite seemed to be present in the air-cooled COAL samples (i.e., #28B and #29B) but not in the water-quenched samples. This anomalous behavior may indicate that other minerals having similar peak identities to chloroapatite are present in air-cooled samples.

The untreated tailings had emanating ^{226}Ra levels of approximately 100 pCi/g, as shown in Table C-VI. For the AVG material heated to 1075-1100°C, the emanating ^{226}Ra was reduced to 0.35 to 0.49 pCi/g, i.e., a reduction factor of 200 to 300. The COAL tailings showed greater emanation reductions at lower temperatures (1050°C), as shown by comparing sample #8 (AVG) with #23 (COAL), where the emanating level of the AVG material was reduced to 1.18 pCi/g compared with 0.33 pCi/g for COAL. A similar comparison at 1000°C between #3E (AVG) and #22 (COAL) shows emanating ^{226}Ra levels of 2.87 and 0.51 pCi/g, respectively. These results are consistent with the hypothesis that the use of coal will cause more reducing conditions during sintering, which may aid in the decomposition of $CaSO_4$. The CaO produced would act as a fluxing agent, increasing the vitreous nature of the thermally stabilized tailings, which would reduce surface area and concomitantly radon emanation. Appendix Figs. C-9 and C-10 are photomicrographs of thin-sectioned TST treated at temperatures from 1000 to 1400°C; cracking and rounding of the large particles are found with increasing temperature. At 1400°C, most of the material has been vitrified; however, some refractory particles are still evident.

The MIX material showed less reduction in emanating ^{226}Ra (factors of ~100), probably because of its heterogeneous nature, with different agglomerates having different compositions and thus different responses to thermal treatment. Another explanation for the decreased effectiveness of thermal stabilization would be that the interior of larger agglomerates did not achieve as high a temperature as did the interior of the smaller agglomerates (AVG and COAL).

The glasses produced at 1525°C showed very large reductions (0.03 to 0.05 pCi/g) in emanating ^{226}Ra, an order of magnitude greater reduction than found at 1100°C.

Longer treatment times did not necessarily produce greater reduction in emanation (compare #27B and C with #28B and C in Table C-VI). Water quenching generally caused greater radon emanation (compare water vs air quenching in Table C-VI). This increase may result from the rapid cooling causing more cracks in the vitrified inclusions or the rehydration of minerals such as anhydrite causing structural damage. Appendix Fig. C-11 shows much more cracking of the vitrified material for the TST, which was water quenched (i.e., rapidly cooled).

These tests, using a batch furnace, indicate that wall temperatures of 1075-1100°C produced materials having substantially reduced emanating power. These materials were no doubt subjected to higher temperature when in contact with the flame; this temperature could not be determined because of limitations in instrumentation. It is probable that in a full-scale coal-fired kiln the tailings materials would not be subjected to a reducing atmosphere as extreme as that produced during treatment of the COAL input; such a kiln would probably have conditions closer to those of the AVG material. At these temperatures (1075 to 1100°C), the handling characteristics of the agglomerates indicated that processing similar to that in cement kilns is feasible with these tailings.

Some of the test run products, as well as untreated materials, were subjected to leaching tests to ascertain changes in leachability and the effect of leaching on

radon emanation. (The leaching procedure is described in Appendix C.) The solids were subjected to ten successive leaches and then analyzed for emanating ^{226}Ra. These results are summarized in Table C-VII. All samples had increased emanating ^{226}Ra levels after leaching; most samples were significantly higher. The smallest increases (10 to 30%) in radon emanation were noted for the thermally stabilized AVG materials. The COAL products (#27B and #27C) show much larger increases (80 to 350%) in emanating ^{226}Ra after leaching. After leaching, the air-cooled (#27B) and water-quenched material (#27C) had similar emanating ^{226}Ra; this would indicate that the higher initial radon emanation of water-quenched material may be more related to the rehydration or dissolution of minerals rather than to the cracking of vitrified material during water quenching. The leaching results in the next section show that the air-cooled material had a high pH ($\sim$10) and much more leachable Al and Si and less leachable Ca, Mg, and SO_4. Thus, the apparently greater aluminosilicate dissolution may cause the substantial radon emanation increase for sample #27B after leaching. It is also possible that #27B may contain more anhydrite because it was not water-quenched and therefore may be subjected to more hydration and resulting structural damage. The thermally stabilized MIX materials show fairly large increases (60 to 180%) in radon emanation after leaching; however, the high-temperature (1100°C) material #20 shows an appreciably smaller increase in emanating ^{226}Ra levels compared with #19 (1050°C). The lower temperature sample #19 shows a pattern of increased Al, Si, Ca, and SO_4, and higher pH than sample #20; thus, greater mineral dissolution is apparent, which could again account for the greater effect of leaching on radon emanation. Higher pH levels may results from residual CaO, which has not reacted with silicates or aluminosilicates during thermal treatment at the lower temperature.

Substantial reductions, i.e., untreated/thermally stabilized ratios $\geqslant 5$, in leachability were found for the following species: SO_4^{-2}, Ca, Mg, Cl, K, F, Mn, Mo, Li, Al, P, Zn, and ^{226}Ra. (The results of leachate analysis are presented in Table C-VIII for the first, fourth, and eighth leaches.) Many elements were present in the thermally stabilized tailings and untreated tailings leachates in concentrations near the analytical detection limits; thus, a number of other elements (Na, U, Pb, As, Ni, Fe, Co, Ba, and B) had reduced leachability, but the magnitude of this reduction is not known. The only element that appeared to have any general increase in leachability caused by thermal stabilization is V; for three test run materials, #14, #15, and #19, substantially more V was leachable from TST than from untreated tailings.

The noncoal AVG and MIX high-temperature (1100°C) materials (#13, #14, and #20) appeared to have less leachable major constituents, i.e., Ca, SO_4, and Mg, than the low-temperature or COAL materials. This may be a result of the more alkaline reaction of the low-temperature or COAL materials with water, i.e., pH >10 for first leaches. The water-quenched #27C COAL leachate did not show such an extreme pH, perhaps because of removal of many alkaline species during quenching. However, substantial quantities of Ca and Mg were still leachable.

Over the 14-day period of 10 successive leaches, there were no apparent trends in pH. The only appreciable change in oxidation-reduction potential was found for the #27B material (COAL input, 1100°C, air cooled), which exhibited a decrease from 360 to 120 mV over the course of the experiment. In general, the untreated and thermally stabilized COAL material formed substantially more reducing leachates (i.e., about 100 mV lower Eh at near-equivalent pH values) than the AVG material. Such reducing conditions may result from sulfides present in the COAL material or formed by the reduction of SO_4^{-2} during the thermal treatments #27B and C. The high pH values for the #27B leachates may have resulted from sulfide production ($S^{-2} + 2H_2O \rightarrow H_2S + 2OH^-$) or the decomposition of sulfates to strongly basic oxides ($CaSO_4 \rightarrow CaO$). Water quenching of hot material would have removed much of the alkaline oxides or sulfides and reduced the alkalinity of this material, #27C, as observed. Leaching under ambient temperature conditions would not be as effective in removing these bases and thus the pH would not decrease readily, as was observed.

In summary, thermal stabilization of tailings has reduced the leachability of most, if not all, of the contaminants analyzed. The TST materials are generally fairly alkaline and oxidized in nature, except for those materials exposed to fairly severe reducing conditions (i.e., COAL input), which tended to have a somewhat reduced character. In general, these results are more encouraging regarding reduced contaminant leachability than the leaching results for the earlier laboratory TST products. This may be caused by increased solid-state mineral reactions during the dynamic thermal treatment (i.e., rotary furnace), as well as exposure to hot flame temperatures.

B. Summary of Pilot-Scale Rotary Furnace Results

The results of the pilot-scale thermal stabilization tests are summarized as follows:

1. A number of elements were enriched in the TST (e.g., Na, Al, V, Mn, U, and Ca) because of the weight lost during dehydration and the decomposition of carbonates, etc.

2. Elements that were volatile and lost during the thermal treatments include Cl, As, Sb, and Se, as well as ^{210}Pb and ^{227}Ac.

3. At temperatures where appreciable sintering was observed (i.e., $\geqslant 1075°C$), radon emanation was generally reduced by more than 99%. The larger (+1/4-in.) heterogeneous agglomerates (MIX input) exhibit smaller reductions in radon emanation at comparable temperatures compared with the homogeneous (AVG) material (+1/8 to 1/2 in.).

4. Leaching caused modest (insignificant) to appreciable (4 times) increases in radon emanation. The thermally stabilized uniform material (AVG) exhibited only slight increases (10 to 30%); the heterogeneous materials (MIX) and those produced under reducing conditions (COAL) were more affected by leaching. Untreated tailings also showed increases in radon emanation as a result of leaching.

5. Leachates of thermally stabilized tailings showed substantial reductions (compared with untreated tailings) in conductivity, SO_4^{-2}, Ca, and many other major and minor aqueous species, including Cl^-, F^-, Mn, Mo, U, Li, Pb, As, Ni, Zn, Co, and ^{226}Ra. The most innocuous leachates were produced by the homogeneous (AVG) material treated at the higher temperatures (1100°C). The pH values of the TST leachates were all basic (i.e., 8.5 to 11.1) compared with the untreated tailings leachates with pH values of 6.5 to 7.5. The oxidation-reduction potentials of the noncoal sample leachates showed oxidizing conditions, whereas the leachates from COAL admixtures were somewhat reducing in character.

C. Engineering and Economic Implications

The pilot-scale rotary furnace test data are consistent with operating a 6-ft-diam by 350-ft-long rotary kiln at 500 ton/day (24 h) even if a residence time of 20 min is required in the kiln. It might be possible to achieve 1000 ton/day with an 8-ft-diam by 350-ft-long kiln. Increased throughput would depend on exit gas velocity and avoiding entrainment of small tailings agglomerates in the gas stream. The costs of pelletizing equipment and operations and air-quenching equipment were not included in the original (1981) calculations (see Appendix B). The savings in capital and operating costs resulting from higher kiln production would be partly offset by these expenses.

Thermodynamic calculations could provide some insight into the fate of volatile elements in the exiting kiln gas stream. Some of these elements might condense on heat recovery (if present) surfaces, flues, or stacks. Others may be removed by scrubber systems used to remove SO_2. Of particular importance regarding corrosion of kiln and flue surfaces are the fate and state of Cl^- lost during thermal stabilization. The design of gaseous emissions control equipment will primarily depend on the amount and state of vaporized sulfur compounds found in the flue gas.

The pilot-scale thermal stabilization results confirm the gross production capacity estimated in the original conceptual engineering design. In addition, these tests have shown that a stabilized tailings product can be produced from a simulated rotary kiln operation. Obviously, the thermal stabilization process cannot be proved technologically effective and cost competitive until more effort is expended on its development. The questions yet unanswered could all be addressed by a combination of *continuous* pilot-plant *kiln* studies and process kinetics/thermodynamics calculations. These activities would need to be performed in parallel to achieve the best information for process design and economic evaluation.

These questions of technology development include the following.

1. What *flame temperature* is actually required?

2. How much excess air is required and how is the air to be divided between primary and secondary air for combustion?

3. What is the maximum practicable heat recovery from cooling of gases and cooling of product?

4. What is the maximum possible throughput for a given diameter of kiln that will avoid excessive entrainment of tailings in the exit gases?

5. What is the effect of kiln length on product characteristics and emissions?

6. What rotational speed and slope are required?

7. Are sulfur compounds (e.g., SO_2) in the off-gas a problem? If so, what kind, how large, and how costly will the sulfur removal equipment be?

8. Will particulate emissions be adequately handled by a venturi scrubber or will baghouses be needed? In place of? In addition to?

9. What happens to volatile contaminants such as Cl, As, Se, ^{210}Pb, ...? What equipment is needed to keep emissions within EPA standards? What does the Cl loss imply about materials of construction of the kiln lining and the off-gas treatment facility and their costs?

10. Will the air-emission treatment facilities reduce radioactivity in the stack gas to acceptable levels? How expensive will it be to reach this point of acceptability?

The small-scale pilot plant results raise the possibility of a considerable *reduction* in the estimated cost of full-scale thermal stabilization operations. Furthermore, the answers to the questions listed above could significantly *decrease or increase* costs. Assuming that high throughput, 50% heat recovery, and moderate sulfur emission controls prove possible, then costs as low as $8.00/ton might be expected in parts of the intermountain West having inexpensive coal deposits as does the Shiprock, New Mexico site. The Shiprock site may require some repiling, if covered in place, because of known pile instability hazards; this situation could make thermal stabilization cost competitive with thick earthen covers because deferred (maintenance) costs of a covered TST pile would be expected to be considerably less than for a covered, repiled, untreated tailings pile. The settling and sliding of the untreated pile may require substantial cover repair in future years, whereas no such need should exist with thermally stabilized tailings.

V. CONCLUSIONS

The technical evaluation of thermal stabilization of tailings has shown that this conditioning method can achieve very great reductions in radon emanation and substantial reductions in leachable contaminants. Pilot-scale tests have indicated that thermal stabilization using rotary kilns appears feasible. Cost estimates of a conceptual coal-fired rotary kiln process are comparable with remedial actions requiring relocation of tailings piles; at the most favorable sites, costs as low as $8.00/ton might be achieved.

Thermal stabilization of tailings appears to be a reasonable remedial action alternative at a few sites where very stringent control of tailings may be required (i.e., in or near population centers). Results indicate that the sintered tailings product will provide long-term immobilization of contaminants without relying on complex barrier systems. It appears that substantial reductions in emanating power result from greatly reduced surface area, mineral transformation and lattice rearrangements, and increased vitreous (amorphous) material sealing or joining mineral grains.

Because of the high costs involved, use of thermal stabilization may only be practical at sites where conventional and less expensive remedial actions will not meet health and environmental protection standards. Actual implemetation of thermal stabilization technology will require an intensive pilot-scale study to quantify process parameters, to determine precise equipment needs, and to finalize operating and capital costs.

APPENDIX A

INITIAL THERMAL STABILIZATION EXPERIMENTS

1. Thermal Treatment Procedures and Results

Both fire clay and graphite crucibles were filled to ~2/3 capacity (100 to 200 g) with the tailings composites. The collection, preparation, and characterization of these composites are described by Dreesen et al. (Vol. I, 1983). The crucibles were loaded into a box furnace that was preheated to 800°C. The furnace reached 1200°C in about 2 h and was kept at temperature for ~3/4 h. The samples were removed about 1-1/2 h later when the temperature of the furnace had decreased to 800°C. The thermally treated tailings are shown in Figs. A-1 through A-15.

The sintered tailings could be broken out of the graphite crucibles and residual graphite removed with a file. Some of the tailings fused to the fire clay crucibles (SHIP Fines, SLC 4AB, DGO LP, DGO SP Fines, and AML Fines); in these cases, the fused tailings and crucible were pulverized together and radon emanation of the combined materials measured. The radon contribution of a control fire clay crucible was determined and found to be negligible at <0.01 pCi/g. All the sintered composites were pulverized to pass through a 6.4-mm (1/4-in.) screen and placed in emanation tubes to measure radon emanation power.

The results of the first experiment on tailings thermal stabilization using SHIP Fines are presented in Table A-I. The emanating ^{226}Ra values of untreated and thermally stabilized tailings composites are reported in Table I.

2. Leaching of Tailings

a. Procedure. Twenty-five grams of each material (–20 mesh) were taken from previously homogenized batches and added to 125 mℓ of deionized water in a polyethylene bottle. These bottles were capped and the mixtures agitated for 24 h in a mechanical shaker vibrating at 160 strokes per minute with a 5-cm stroke length. The resultant slurries were filtered through 0.45-μm filters and the filtrate saved for analysis. The third rinse was saved, the first two discarded. When necessary, high-speed centrifugation was used to separate solids from liquids but was always followed by filtration, as described above.

b. Analytical Techniques for Leachates. Analytical sensitivity and measurement precision are such that flame atomic absorption spectrometry (AAS) methods are suitable for the determination of Cd, Cr, Pb, and Ag, as well as many other substances present in the leachates. Inductively coupled argon plasma spectrometry (ICP) proved to be superior to AAS for determination of Ba, Mo, and in most cases, As and Se. In a few samples (those containing several hundred ppm of calcium), the low levels of As and Se could not be satisfactorily determined by ICP. For these few samples, graphite furnace atomic absorption (GFAA) was employed after preliminary cation removal with Dowex 50x8 cation exchange resin. Uranium was determined by laser fluorimetry (LF) using a Scintrex UA-3 uranium-specific fluorimeter. Anion measurements were done by ion chromatography (IC), using a Dionex Model 16 instrument with standard columns and eluent. The flame AAS and ICP measurements were performed with a Perkin-Elmer Model 5000 ICP instrument, and the GFAA work employed a Perkin-Elmer Model 460 fitted with graphite furnace unit HGA-2100. Details regarding design of analysis procedures and analytical methods are presented in the next section.

c. Design of Trace Element Analysis Procedures for Leachates. In establishing standards for which testing is required, it is customary to establish a "consumer's risk" (error of the second kind, or β-error), which one is willing to accept. This is the risk that the test result does not lead to a "true" conclusion as to whether the tested material conforms to the specification. This kind of error is established by the test conditions, particularly the number of independent replicate tests performed. Thus, for example, it would be prudent to specify that analysis results suggesting compliance with the standards should not be "untrue" in more than 5%, or 10%, or some other pre-established percentage of cases. With this specification, it is possible to prepare a sampling and analysis plan that can unambiguously be shown to operate as required.

For the purposes of the present study, we have chosen to work as though the "consumer's risk" of an untrue answer had been specified at the 5% level and to

Note:
Figs. A-1 through A-15 show tailings heat treated at 1200°C.
Oxidizing conditions—fire clay crucible.
Reducing conditions—graphite crucible.

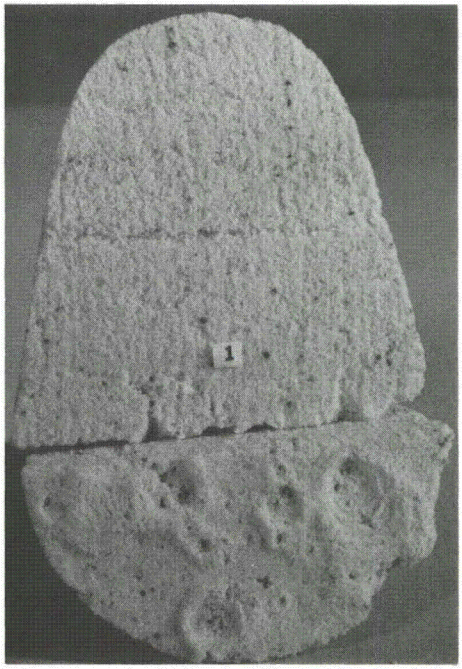

Fig. A-1. SHIP Sands—oxidizing conditions.

Fig. A-2. SHIP Fines—oxidizing conditions.

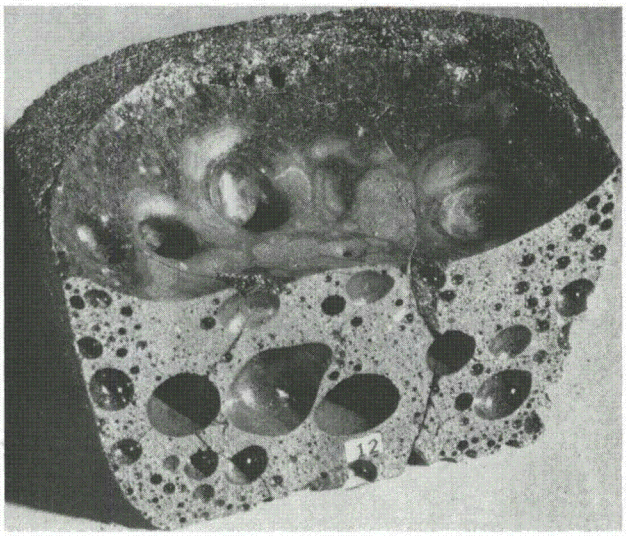

Fig. A-3. SHIP Fines—reducing conditions.

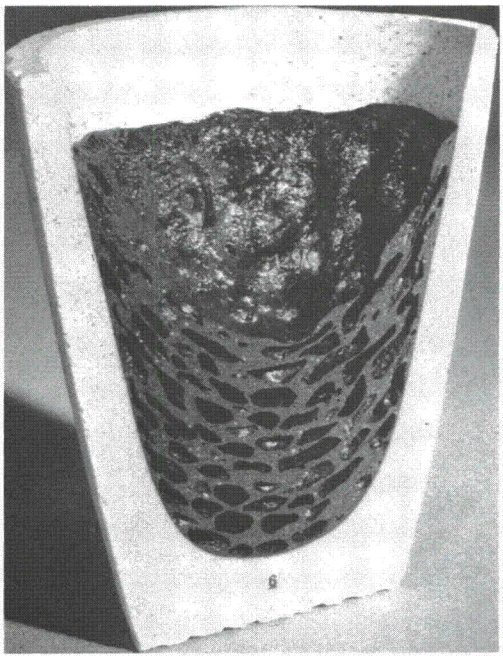

Fig. A-4. DGO LP—oxidizing conditions.

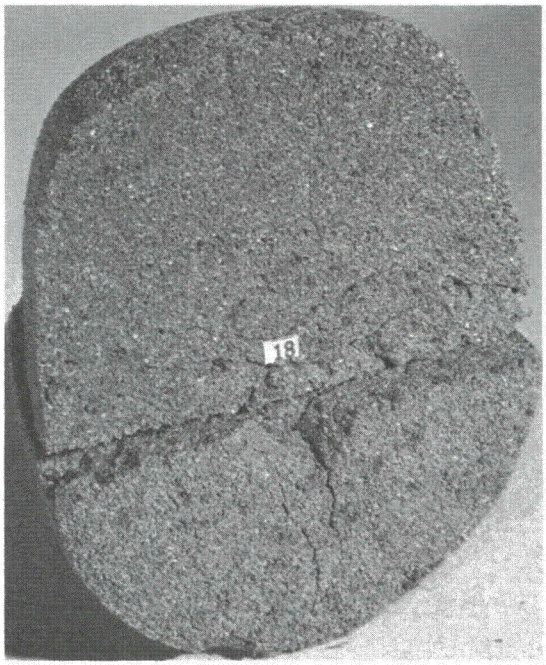

Fig. A-5. DGO SP Sands—reducing conditions.

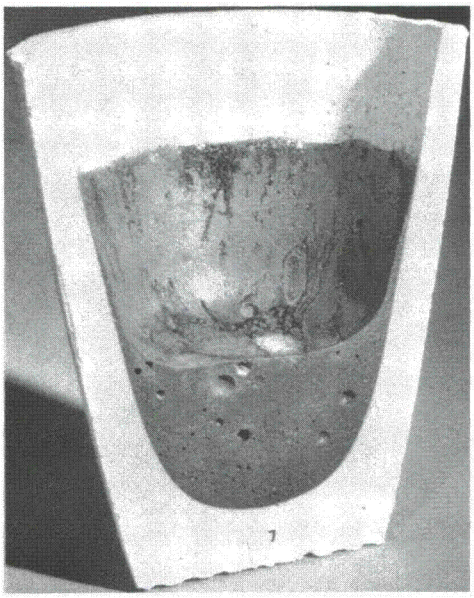

Fig. A-6. DGO SP Fines—oxidizing conditions.

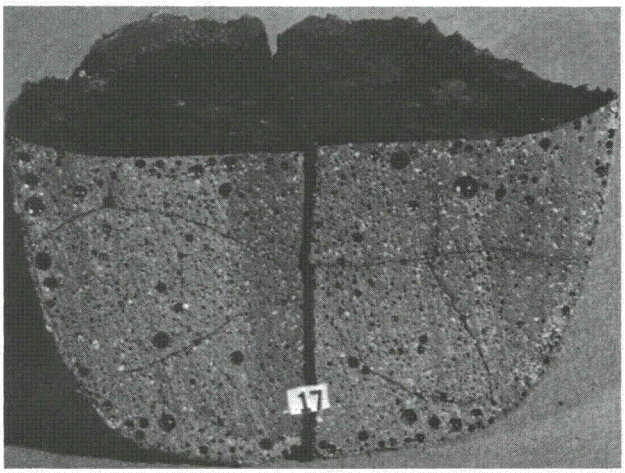

Fig. A-7. DGO SP Fines—reducing conditions.

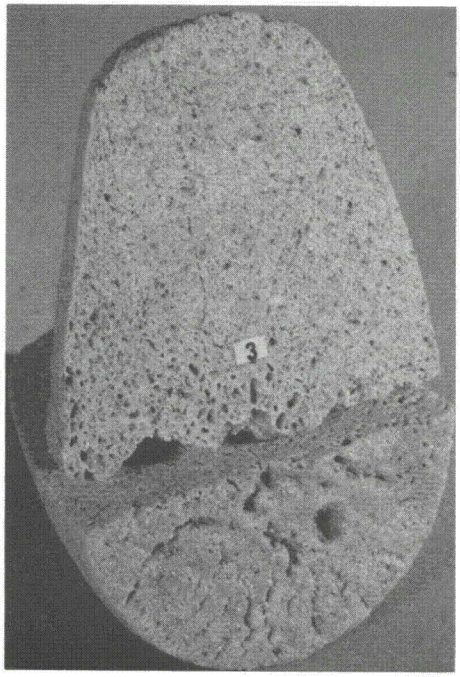

Fig. A-8. SLC 1AB—oxidizing conditions.

Fig. A-9. SLC 1AB—reducing conditions.

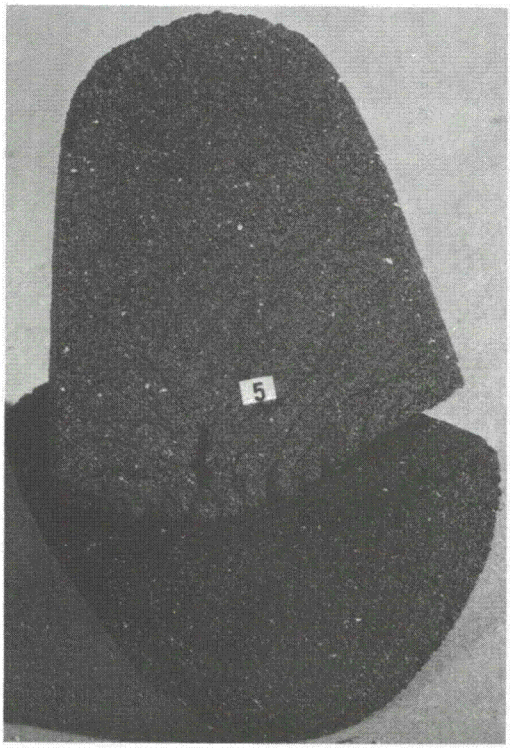

Fig. A-10. SLC 5AB—oxidizing conditions.

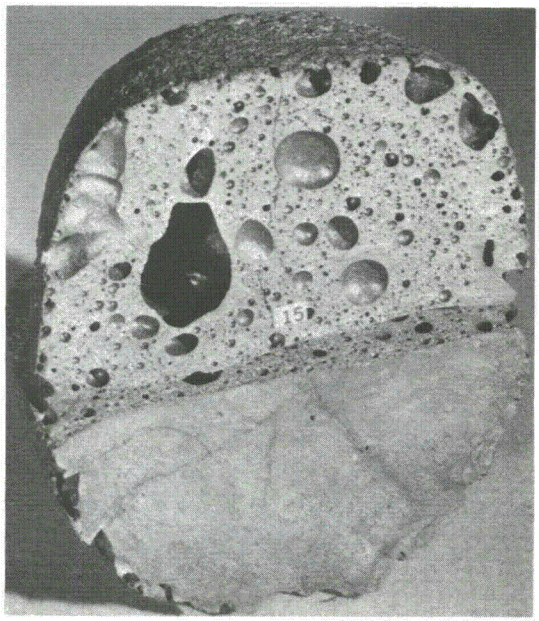

Fig. A-11. SLC 5AB—reducing conditions.

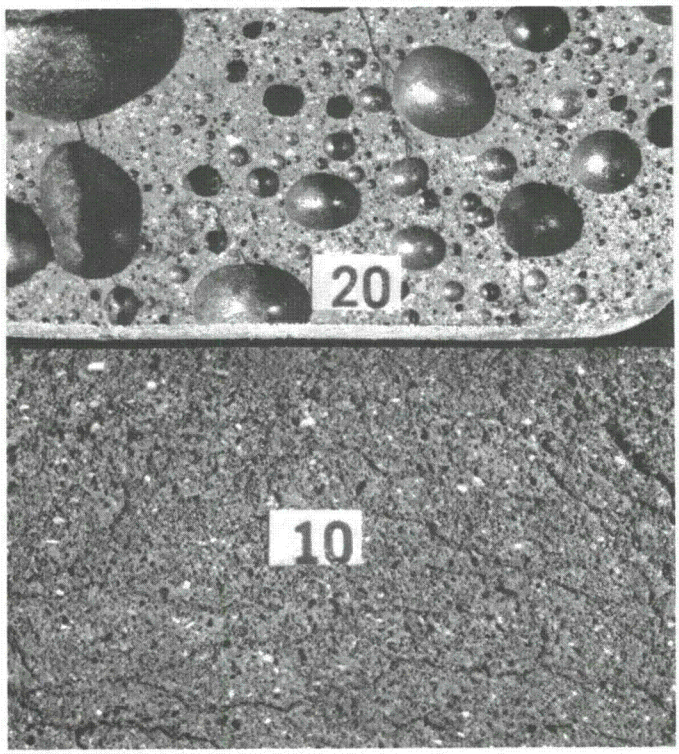

Fig. A-12. SLC 5AB—reducing conditions (upper), oxidizing conditions (lower).

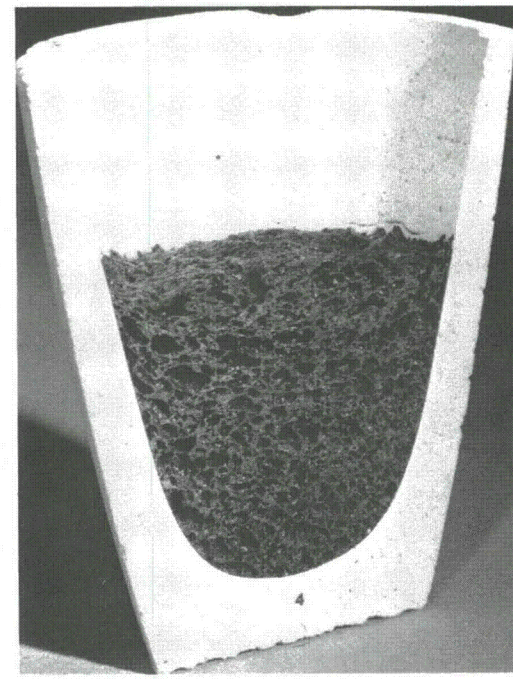

Fig. A-13. SLC 4AB—oxidizing conditions.

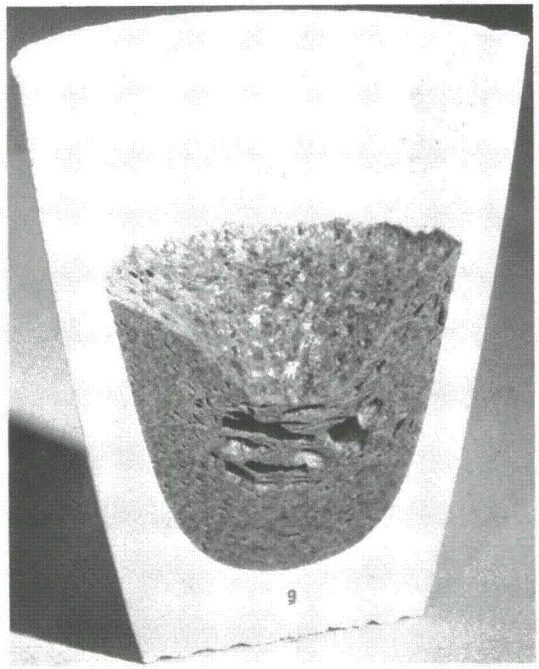

Fig. A-14. AML Fines—oxidizing conditions.

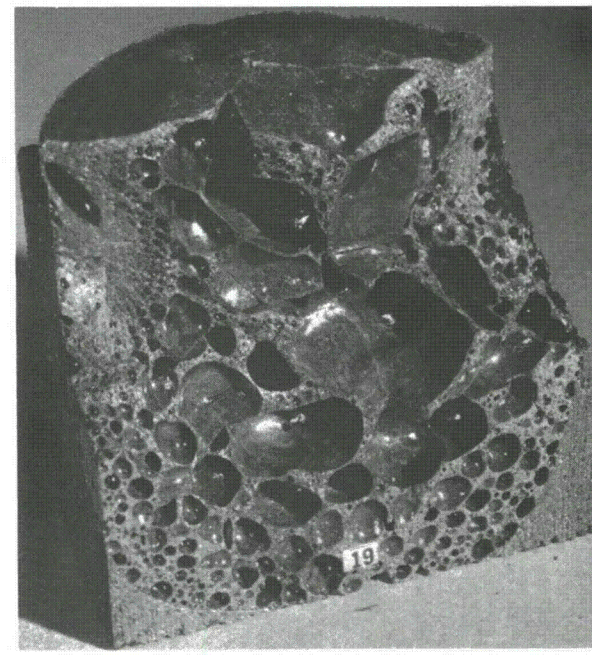

Fig. A-15. AML Fines—reducing conditions.

TABLE A-I

INFLUENCE OF HIGH TEMPERATURE TREATMENTS ON THE EMANATING POWER OF SHIP FINES TAILINGS COMPOSITE

Site	Composite	Temperature Treatment (°C)	Emanating ^{226}Ra (pCi/g)[a]	Emanation Coefficient (%)	Reduction in Emanation Power (%)
			No Additives		
SHIP	FINES	1150	2.5 ± 0.8 (n=3)	0.2	99
		1050	11 ± 2 (n=3)	0.9	95
		950	28 ± 7 (n=3)	2	87
		850	107 ± 23 (n=3)	9	50
		750	110 ± 15 (n=3)	9	49
		Untreated	214 ± 5 (n=9)	17	0
			Flux 5% NaOH		
SHIP	FINES	1150	1.5 ± 1.0 (n=4)	0.1	99

[a]Mean ± 1 standard deviation.

perform the analysis accordingly. In this way it was possible to establish that practicable methods exist for the determination of ten of the eleven regulated substances that are amenable to chemical analysis. (Mercury was not determined because of the low probability of its presence in materials sintered at 1200°C. Uranium was determined by a chemical method in which the concentration equivalent of 10.0 pCi/ℓ (0.03 ppm) was used as the specification limit. Radium was determined by a separate radiochemical procedure. In addition to regulated elements, several other substances were determined for purposes of further evaluating the proposed conditioning process.

Testing for compliance with the specification limit employed a single-sided t-test at the 95% confidence level ($\alpha = 0.05$) with the number of independent replicate measurements per sample (n_s) adjusted so that the β-error was equal to or less than 0.05. The t-test was used because it was felt that inadequate information was available to evaluate the standard deviation parameter, σ. In most cases, six statistically independent measurements were performed, with readjustment of baseline and calibration standards between replicate measurements. A series of "blank" measurements was obtained using water purified in a commercial ion exchange purification system (Milli-Q).

The β-error compliance was then tested at the specification limit by use of operating characteristic curves for the one-sided t-test, $\alpha = 0.05$. Analytical methods and conditions used for the regulated species are given in Table A-II.

Detection limits and standard deviation estimates were computed using a method for comparing a test-sample mean with a blank mean when σ is unknown and must be estimated from the samples. The two-sided 95% confidence limits were also computed where appropriate.

For the GFAA work, a slightly different calculation procedure was employed. Four successive sample measurements and four following spiked-sample measurements were used to compute the reported results by the standard addition method. Because of the generally poorer reproducibility of GFAA measurements, use of this technique often results in only a slight improvement in detection limits compared with "favorable case" AAS or ICP, unless an inordinate expenditure of analysis time is made. GFAA is, however, preferable to ICP for near-detection-limit samples because it is much less subject to the large biases caused by background and interference-element radiation that occasionally arise in ICP work. The ICP technique is most advantageous with samples having simple matrix composition.

TABLE A-II

METHODS FOR ANALYZING EPA GUIDELINE ELEMENTS IN URANIUM MILL TAILINGS LEACHATES

Element	Method	Detection Limit[a] (mg/ℓ)	Wavelength (nm) [Conditions]
Arsenic	ICP	0.003	189.0
Arsenic	GFAA	0.002	193.7 [Remove metals with Dowex 50x8]
Barium	ICP	0.003	455.4
Cadmium	AAS	0.001	228.8 [C_2H_2 - air][c]
Chromium	AAS	0.004	357.9 [C_2H_2 - air][c]
Lead	AAS	0.006	217.0 [C_2H_2 - air][c]
Molybdenum	ICP	0.004	202.0
Nitrogen	IC	ND[b]	[0.003M $NaHCO_3$, 0.0024M Na_2CO_3][d]
Selenium	ICP	0.007	196.0
Selenium	GFAA	0.006	196.0 [Remove metals with Dowex 50x8]
Silver	AAS	0.003	328.1 [C_2H_2 - air][c]
Uranium	LF	0.0001	[10% H_3PO_4, remove chloride]

[a]Based on 6 to 10 blank measurements and 4 to 6 sample measurements.
[b]Not determined, estimated <2 ppm under conditions employed.
[c]Type of flame.
[d]Eluent.

In addition to the EPA-specified elements, 14 additional substances and the pH were determined in the leachates. Methods of comparable reliability were employed and were found to operate easily with the mill tailings leachates. Analysis conditions found to be satisfactory are presented in Table A-III. In general, the flame AAS technique is preferred, except for those elements having very much more favorable ICP characteristics. The latter generally include those elements that tend to form very stable oxides under AAS flame conditions. An exception to this rule is the determination of vanadium in the tailings leachates. This element is normally determined by ICP with an advantage of approximately 10X in signal-to-noise ratio compared with AAS, but for an undetermined reason, the signal-to-noise ratio in these particular samples was not acceptable. The determination was performed easily by flame AAS.

d. Results and Interpretation of Initial Leaching Experiment. The results of the leaching experiment are presented in Table A-IV for the elements in the proposed EPA water standards and in Table A-V for other important major, minor, and trace species in these leachates.

At least four mechanisms may contribute to the apparent diminished leachability of sintered tailings:

(1) metathetic formation of new compounds of increased thermodynamic stability or kinetic inertness;

(2) thermal decomposition of sulfates (e.g., $MgSO_4$) to form basic oxides, which in turn become the dominant factor in control of leachate pH;

(3) volatilization of certain constituents (e.g., chloride as HCl, sulfate as SO_3 or H_2SO_4, selenium as the element or oxide); and

(4) depletion by volatilization of complex ion formers such as carbonate (as CO_2), resulting in decreased chemical potential for solubilization of uranyl as its carbonate complex.

The strong correlation between leachate pH and soluble constituent concentration leads us to believe that the second mechanism, thermal decomposition of sulfates, may be the most significant of the four. The observed solubilities of the trace metals in some untreated tailings leachates can be attributed largely to the low pH (high acidity) of the solutions, which in turn is related to the hydrolysis of aluminum and iron (III)

TABLE A-III

METHODS FOR ANALYZING OTHER ELEMENTS IN URANIUM MILL TAILINGS LEACHATES

Element	Method	Detection Limit (mg/ℓ)	Wavelength (nm) and Conditions
Boron	ICP	0.002	249.8
Iron	AAS	0.009	248.3
Manganese	AAS	0.01	279.5
Nickel	AAS	0.01	232.0
Zinc	AAS	0.003	213.9
Vanadium	AAS	0.10	318.4 [C_2H_2/N_2O][a]
Phosphate (PO_4^{-3})	ICP	0.05	213.6
Silica (SiO_2)	AAS	ND	251.6 [1000 ppm Na^+][b]
Sodium	AAS	ND	589.0 [1000 ppm Cs^+][b]
Calcium	AAS	ND	422.7 [1000 ppm La^{+3}, C_2H_2/air][a]
Chloride	IC	ND	[0.003M $NaHCO_3$/0.0024M Na_2CO_3][c]
Sulfate	IC	1.0	[0.003M $NaHCO_3$/0.0024M Na_2CO_3][c]
Magnesium	AAS	ND	285.2 [C_2H_2/air][a]
Aluminum	AAS	ND	309.3 [C_2H_2/N_2O][a]

[a]Type of flame.
[b]Matrix adjustment.
[c]Eluent

ND = not determined.

sulfate salts and residual sulfuric acid present in the tailings. Contact of tailings with water continues to produce acidic leachates for as long as soluble iron or aluminum remains. This occurs below pH ~4; above this pH, essentially all of the iron and aluminum will have precipitated. The solution pH control is then transferred to other substances, such as the bicarbonate, which are present in the tailings or in natural waters. The other major constituents of the untreated tailings leachates (magnesium, sodium, calcium) will have minor effect on the leachate pH, which is expected to remain acidic, causing many metal ions to remain soluble to environmentally significant extents.

Thermal treatment of uranium tailings in an open system results in conversion of the sulfate salts of iron and aluminum (as well as some of the other transition metals present) to oxides by reactions that continue to completion above 800°C. Conversion of oxides to silicates may simultaneously occur. Thus, the water leaching of thermally treated tailings cannot be controlled by the acid release accompanying hydrolysis of iron or aluminum ions. The controlling reactions are determined by other major constituents. Since calcium and sulfate are the dominant ionic species present in the leachates, they will, to a large extent, determine the overall solution properties. This may be seen from consideration of the sulfate/calcium ratios observed for the untreated and treated materials compared with the leachate pH values. This information is presented in Table A-VI. Note that in either gypsum ($CaSO_4 \cdot 2H_2O$) or anhydrite ($CaSO_4$), the stoichiometric mass ratio of sulfate to calcium is 2.40. Positive deviations from this ratio account for the sulfate (or perhaps bisulfate) from iron and aluminum sulfates or sulfuric acid at very low pH and correspond to increased solubilization of trace metals. Dissolved silica (silicic acid) may be safely neglected in the acidic and neutral leachates because the predominant form of this substance is the neutral monomer at pH levels below 8.

The thermal stability of $CaSO_4$ is such that no appreciable volatilization of SO_3 would be expected under oxidizing conditions, even at 1200°C. Magnesium

TABLE A-IV

LEACHATE COMPOSITION OF UNTREATED TAILINGS AND TAILINGS SINTERED AT 1200°C — EPA GUIDELINE ELEMENTS

				Leachate Concentration (mg/ℓ except ^{226}Ra in pCi/ℓ)			
Tailings	Composite	Treatment[a]	pH	^{226}Ra	As	Ba	Cd
DGO	SP	U	8.1	66 ± 3	0.42 ± 0.03	0.25 ± 0.01	<0.001
	Sands	1200	7.9	9 ± 1	0.032 ± 0.015	0.004 ± 0.006	<0.002
DGO	SP	U	8.0	20 ± 1	0.61 ± 0.01	0.06 ± 0.01	<0.002
	Fines	1200	7.8	13 ± 2	0.05 ± 0.01	0.46 ± 0.01	<0.002
DGO	LP	U	8.8	10 ± 1	0.24 ± 0.01	0.062 ± 0.004	<0.001
		1200	8.2	7 ± 1	0.018 ± 0.002	0.020 ± 0.003	<0.001
SHIP	Sands	U	3.7	33 ± 4	0.23 ± 0.05	0.042 ± 0.005	0.042 ± 0.002
		1200	9.2	61 ± 6	1.38 ± 0.08	0.34 ± 0.004	<0.002
SHIP	Fines	U	3.2	32 ± 5	0.004 ± 0.01	0.03 ± 0.01	0.088 ± 0.008
		1200	6.8	40 ± 2	0.002 ± 0.002	0.14 ± 0.03	<0.005
		Glass (1400°)	9.8	6 ± 1	0.020 ± 0.004	0.013 ± 0.007	<0.002
SLC	1AB	U	3.3	71 ± 7	0.009 ± 0.002	0.037 ± 0.002	0.08 ± 0.01
		1200	8.2	21 ± 1	0.04 ± 0.02	0.47 ± 0.07	<0.003
SLC	4AB	U	2.6	88 ± 7	0.76 ± 0.05	0.025 ± 0.005	0.16 ± 0.02
		1200	6.6	42 ± 4	0.05 ± 0.01	0.12 ± 0.03	0.003 ± 0.001
SLC	5AB	U	7.5	10 ± 2	1.10 ± 0.20	0.013 ± 0.004	<0.002
		1200	7.9	3 ± 1	0.031 ± 0.003	0.005 ± 0.003	<0.002
AML	Fines	U	9.1	264 ± 4	1.03 ± 0.07	0.03 ± 0.01	<0.002
		1200	7.5	3 ± 1	0.01 ± 0.01	0.009 ± 0.002	<0.002
EPA Guideline				5	0.05	1	0.01

[a]U = untreated.
1200 = thermal treatment at 1200°C in fire clay crucible.

TABLE A-IV (cont)

Tailings	Composite	Treatment[a]	Leachate Concentration (mg/ℓ except ^{226}Ra in pCi/ℓ) Cr	Mo	Pb	Se	U
)GO	SP	U	<0.004	0.03 ± 0.01	<0.04	0.27 ± 0.03	0.83
	Sands	1200	<0.004	0.89 ± 0.06	<0.05	0.04 ± 0.01	0.015
)GO	SP	U	<0.004	0.28 ± 0.02	<0.01	0.46 ± 0.02	1.8
	Fines	1200	<0.004	0.07 ± 0.01	<0.01	0.04 ± 0.01	0.007
)GO	LP	U	0.05 ± 0.01	0.012 ± 0.002	<0.03	0.09 ± 0.01	0.16
		1200	<0.004	0.019 ± 0.004	<0.01	0.03 ± 0.01	0.0003
HIP	Sands	U	<0.004	0.06 ± 0.01	0.40 ± 0.05	0.48 ± 0.07	0.90
		1200	0.036 ± 0.003	0.69 ± 0.10	<0.04	0.07 ± 0.01	0.001
HIP	Fines	U	<0.004	0.10 ± 0.02	0.36 ± 0.05	0.33 ± 0.03	0.73
		1200	<0.004	0.47 ± 0.03	<0.01	0.15 ± 0.04	0.002
		Glass (1400°)	<0.004	0.02 ± 0.01	<0.04	0.02 ± 0.01	0.001
LC	1AB	U	<0.004	0.027 ± 0.003	0.08 ± 0.03	<0.01	8.5
		1200	0.016 ± 0.005	0.82 ± 0.006	<0.01	<0.01	0.017
LC	4AB	U	0.30 ± 0.02	2.05 ± 0.09	1.67 ± 0.08	0.57 ± 0.03	1.22
		1200	<0.04	1.92 ± 0.15	<0.01	<0.01	0.008
LC	5AB	U	<0.004	1.53 ± 0.05	<0.01	0.07 ± 0.03	0.005
		1200	<0.004	0.83 ± 0.02	<0.01	<0.01	0.0007
ML	Fines	U	<0.004	0.84 ± 0.03	0.02 ± 0.01	1.27 ± 0.02	0.21
		1200	<0.004	<0.004	<0.01	<0.01	0.002
PA Guideline			0.05	0.05	0.05	0.01	0.03

U = untreated.
1200 = thermal treatment at 1200°C in fire clay crucible.

TABLE A-V

LEACHATE COMPOSITION OF UNTREATED TAILINGS AND TAILINGS SINTERED AT 1200°C

				Leachate Concentration (mg/ℓ)													
Tailings	Composite	Treatment[a]	pH	SO_4^{-2}	Ca	SiO_2	Na	Cl^-	Mg	Fe	V	PO_4^{-3}	Al	Zn	Mn	B	Ni
DGO	SP	U	8.1	570	240	51	6	1	8.4	<0.03	8.0	0.9	<0.1	<0.01	0.01	0.012	<0.01
	Sand	1200	7.9	11	5	18	6	2	0.5	0.08	1.0	0.3	0.2	<0.01	<0.01	0.06	<0.01
DGO	SP	U	8.0	1100	450	46	25	–	22.5	<0.04	11.0	3.7	0.2	0.02	0.28	0.42	<0.01
	Fines	1200	7.8	170	63	8	19	2	1.9	<0.01	0.5	0.2	<0.1	<0.01	<0.01	0.01	<0.01
DGO	LP	U	8.8	9	16	11	22	4	6.4	<0.01	8.9	2.6	<0.1	<0.01	<0.01	0.09	<0.01
		1200	8.2	12	5	14	6	1	1.1	0.02	0.6	1.7	<0.1	<0.01	<0.01	0.015	0.01
SHIP	Sand	U	3.7	1600	580	46	14	–	21.5	0.20	0.2	1.3	3.0	0.62	0.67	0.059	0.10
		1200	9.2	175	80	24	3	3	0.6	<0.06	0.9	0.2	<0.1	<0.01	<0.01	0.060	<0.05
SHIP	Fines	U	3.2	2000	470	63	66	2	91	2.5	2.0	0.9	16	1.16	3.1	0.19	0.80
		1200	6.8	1700	650	5	1	–	1.2	<0.04	<0.1	<0.1	<0.1	<0.01	0.01	0.08	<0.01
		Glass (1400°)	9.8	1	7	53	12	0.4	0.5	0.04	0.4	0.2	0.3	<0.01	<0.01	2.3	<0.01
SLC	1AB	U	3.3	1600	550	54	3	–	11.8	0.73	<0.1	1.6	11	2.8	2.8	0.17	0.63
		1200	8.2	950	350	15	2	2	0.4	<0.01	<0.1	1.2	0.1	<0.01	<0.01	0.04	<0.01
SLC	4AB	U	2.6	3370	520	76	340	380	94	52	6.1	9.3	12	11.9	7.6	0.16	1.63
		1200	6.6	460	170	7	2	6	1.0	0.04	<0.1	<0.1	<0.1	0.01	<0.01	0.02	<0.01
SLC	5AB	U	7.5	1700	550	81	140	42	41.3	<0.01	33	8.4	<0.1	<0.01	0.37	0.35	0.18
		1200	7.9	7	8	16	6	2	0.6	<0.01	1.7	9.6	<0.1	<0.01	<0.01	0.43	<0.01
AML	Fines	U	9.1	76	4	43	130	6	0.2	2.2	1.8	1.1	<0.1	0.01	<0.01	0.41	<0.01
		1200	7.5	56	22	12	3	3	0.7	0.04	<0.3	<0.1	<0.1	<0.01	<0.01	0.04	<0.01

[a]U = *untreated.*
1200 = thermal treatment at 1200°C in fire clay crucibles.

TABLE A-VI

SULFATE/CALCIUM RATIOS AND pH OF UNTREATED (U) AND SINTERED (1200°C) TAILINGS LEACHATES

Leachate	pH	SO_4/Ca[a]	Fe + Al Conc (mg/ℓ)
DGO SP Sands			
(U)	8.1	2.4	
(1200)	7.9	2.2	
DGO SP Fines			
(U)	8.0	2.4	
(1200)	7.8	2.7	
DGO LP			
(U)	8.8	0.6	
(1200)	8.2	2.4	
SHIP Sands			
(U)	3.7	2.8	3
(1200)	9.2	2.2	
SHIP Fines			
(U)	3.2	4.3	19
(1200)	6.8	2.6	
SLC 1AB			
(U)	3.3	2.9	12
(1200)	8.2	2.7	
SLC 4AB			
(U)	2.6	6.5	64
1200	6.6	2.7	
SLC 5AB			
(U)	7.5	3.1	
(1200)	7.9	0.9	
AML Fines			
(U)	9.1	19	
(1200)	7.5	2.5	

[a]Mass ratio for gypsum and anhydrite: $SO_4/Ca = 2.40$.

sulfate, however, does decompose to an oxide at slightly over 1100°C. [Actually, the probable form of magnesium sulfate in tailings is epsomite ($MgSO_4 \cdot 7H_2O$), which is known to decompose to basic salts at much lower temperatures.] For the dissolution of hydrous magnesium oxide, the solubility product constant is approximately 9×10^{-12}. From this solubility product value, magnesium hydroxide is seen to be quite soluble in acid solutions but, in the absence of acid, accepts protons from water to produce a solution pH of 8 to 9. In this pH region, interaction of Mg^{++} with dissolved silica species rapidly increases with increasing pH, and the various magnesium silicates precipitate to limit the pH to about 9. Magnesium *sulfate*, on the other hand, is quite soluble and is unlikely to control or be controlled by the sulfate concentration level in either untreated or sintered tailings leachates.

The data thus suggest that the sulfate level in thermally treated tailings leachates is controlled by the solubility of gypsum or anhydrite, whereas the pH may be controlled jointly by silicic acid and $Mg(OH)_2$ formed by thermal decomposition of $MgSO_4 \cdot 7H_2O$ or related salts. The transition metal concentrations are controlled by the pH of the leachate. Barium and radium solubility will be controlled by the soluble sulfate level. The latter conclusion is not especially favorable for the satisfactory long-term disposal of this form of sintered tailings. If exposed to water, the calcium sulfate may eventually be depleted to the point at which barium and radium dissolution is no longer inhibited by the presence of high sulfate that originates from the solubility of $CaSO_4$, although it is possible that Ba/Ra dissolution would be slow enough to keep contaminant release rates within acceptable limits. Final disposal under dry conditions is thus preferable for optimal long-term assurance of radium retention in thermally conditioned tailings dominated by anhydrite. Alternative sintering processes could produce thermally stabilized tailings having a mineral assemblage that would limit radium leachability.

Molybdenum control represents a special case in which, under the prevailing alkaline conditions, the element must be present as the molybdate anion or as some complex such as phosphomolybdate. The molybdate ion level might be expected to be controlled by the calcium ion level in the leachates, since calcium molybdate, $CaMoO_4$, is fairly insoluble ($K_{sp} = 10^{-8}$). In addition, molybdate might either control or be controlled

by the lead level in the solution, since for $PbMoO_4$, $K_{sp} = 10^{-13}$. The effect of calcium can be estimated from the following calculated results, which assume equilibrium and ionic strength established by the calcium and corresponding sulfate levels:

Calcium (ppm)	Expected Molybdenum (ppm)
1300	0.18
400	0.6
40	1.8
4	12

Thus free calcium ion concentrations must be very high to adequately control molybdenum concentrations. Comparison with the actual data shows that most of the solutions are undersaturated with respect to molybdenum at the observed calcium levels, showing that calcium cannot be controlling molybdenum levels.

APPENDIX B

TECHNOECONOMIC ANALYSIS OF THERMAL STABILIZATION*

1. Cost Analysis (as of Summer 1981)

Cost estimates for thermal stabilization of tailings at Salt Lake City, Shiprock, and Canonsburg were calculated and the results summarized in Tables B-I, B-II, B-III, and B-IV. In comparing the tables we can see that thermal stabilization, as in the conceptual process, is quite energy intensive. Therefore, at Shiprock where both coal and electricity costs are quite low, the cost per ton for thermal stabilization is about the same as for moving the pile a relatively short distance, but more than covering the same pile in place with earth. The thermal stabilization option has a relatively high labor cost, but, if applied in place as contemplated, other very expensive labor costs are avoided. These are the costs of environmental impact studies, radiological monitoring in transport, and site decontamination, which are incurred if the pile is to be moved from its original location. Thus, while the per ton cost for a small (but presumably highly radioactive) pile like Canonsburg appears quite high, it may be no more expensive than moving the pile through a densely populated area. Thus, the high cost of thermally stabilizing tailings may not result in an overall cost disadvantage compared with other remedial actions.

a. Salt Lake City Site. Cost information [(Ford, Bacon & Davis Utah Inc., 1981) and Baird 1981**] updated to current costs and standards (1981) is complete for the Salt Lake City site. This site provides a convenient vehicle for the comparison of earth cover in place, asphalt cover in place, and thermal stabilization in place.

A comparison of the estimated costs of alternative remedial actions at Vitro site is given in Table B-V. Thermal stabilization (Option I-T) is comparable in cost with options II-A and IV, which require relocation of the tailings. These options are all about twice as expensive as cover-in-place options (I and I-P); however, certain long-term deferred costs were not included in this analysis.

Calculated on a per ton basis, thermal stabilization costs nearly twice as much at Vitro site as it does at Shiprock. The figures are $15.89/ton for Shiprock and $29.07/ton for Salt Lake City. The primary reason for this difference is the cost of coal at the two locations. The coal available at Salt Lake City is a higher grade, sells for more at the mine mouth, and must be trucked over 120 miles; the coal used at Shiprock is of a slightly lower grade, sells at a considerably lower price at the mine mouth, and must be trucked only 26 miles.

*Calculations based on short tons.

**This information provided by R. D. Baird, Ford, Bacon & Davis Utah Inc.

TABLE B-I

SUMMARY OF COSTS FOR REMEDIAL ACTION USING THERMAL STABILIZATION VITRO SITE @ 500 TON/DAY

Item	Total Cost ($)	Cost per Ton ($)
1. Capital Expense[a]	3 750 000	1.43
2. Direct Labor and Benefits[b]	14 304 000	5.47
3. Coal, delivered	12 107 000	4.63
4. Electricity @ $0.05/kWh	1 883 000	0.72
5. Misc. Oper. Exp., incl. cover[c]	3 530 000	1.35
6. Wind-blown & Off-Site Remedial	13 500 000	5.16
7. Contractor indirect (30% of 2, 5, & 6)	9 402 000	3.60
8. Estimated total direct & indirect	58 480 000	22.36
9. Contingency (30% of Line 8)	17 540 000	
10. Grand Total	76 020 000	29.07

[a]Kiln, auxiliaries, dust collection, conveyors, including enginering and contractor charges. Based on *used* kiln. Possible salvage value not calculated.
[b]See Table B-VII
[c]Does not include flue gas desulfurization. Add $1.30 per ton, if required.

TABLE B-II

SUMMARY OF COSTS FOR REMEDIAL ACTION USING THERMAL STABILIZATION SHIPROCK SITE @ 500 TON/DAY

Item	Total Cost ($)	Cost per Ton ($)
1. Capital Expense[a]	3 750 000	2.21
2. Direct Labor and Benefits[b]	8 364 000	4.92
3. Coal, delivered	2 363 000	1.39
4. Electricity @ $0.04/kWh	979 000	0.56
5. Misc. Oper. Exp., incl. cover[c]	2 159 000	1.27
6. Wind-blown & Off-Site Remedial	d	d
7. Contractor indirect (30% of 2, 5, & 6)	3 162 000	1.86
8. Estimated total direct & indirect	20 780 000	12.22
9. Contingency (30% of Line 8)	6 234 000	
10. Grand Total	27 014 000	15.89

[a]Kiln, auxiliaries, dust collection, conveyors, including engineering & contractor charges. Based on *used* kiln. Possible salvage value not calculated.
[b]See Tables B-VII and B-VIII.
[c]Does not include flue gas desulfurization. Add $1.30 per ton, if required.
[d]Not calculated for this site.

TABLE B-III

SUMMARY OF COSTS FOR REMEDIAL ACTION USING THERMAL STABILIZATION SHIPROCK SITE @ 1000 TON/DAY

Item	Total Cost ($)	Cost per Ton ($)
1. Capital Expense[a]	6 750 000	3.97
2. Direct Labor and Benefits[b]	5 883 000	3.46
3. Coal, delivered	2 363 000	1.39
4. Electricity @ $0.04/kWh	979 000	0.56
5. Misc. Oper. Exp., incl. cover[c]	2 459 000	1.45
6. Wind-blown & Off-Site Remedial	d	d
7. Contractor Indirect (30% of 2, 5, & 6)	2 502 000	1.47
8. Estimated total direct & indirect	20 936 000	12.32[e]
9. Contengency (30% of Line 8)	6 280 000	
10. Grand Total	27 216 000	16.01[e]

[a]Kiln, auxiliaries, dust collection, conveyors, including engineering and contractor charges. Based on *used* kiln. Possible salvage value not calculated.
[b]See Table B-VIII.
[c]Does not include flue gas desulfurization. Add $2.30 per ton, if required.
[d]Not calculated for this site.
[e]Calculated from Col. 1 totals. Col. 2 does not add precisely because of rounding.

TABLE B-IV

SUMMARY OF COSTS FOR REMEDIAL ACTION USING THERMAL STABILIZATION CANONSBURG SITE @ 300 TON/DAY

Item	Total Cost ($)	Cost per Ton ($)
1. Capital Expense[a]	3 200 000	16.00
2. Direct Labor and Benefits[b]	1 094 000	5.47
3. Coal, delivered	1 194 000	5.97
4. Electricity @ $0.07/kWh	200 000	1.00
5. Misc. Oper. Exp., incl. cover[c]	254 000	1.27
6. Wind-blown & Off-Site Remedial	d	d
7. Contractor indirect (30% of 2, 5, & 6)	404 000	2.02
8. Estimated total direct & indirect	6 346 000	31.73
9. Contingency (30% of Line 8)	1 904 000	
10. Grand Total	8 250 000	41.25

[a]Kiln, auxiliaries, dust collection, conveyors, including engineering and contractor charges. Based on *used* kiln. Possible salvage value not calculated.
[b]Same as Table B-VII.
[c]Does not include flue gas desulfurization. Add $2.00 per ton, if required.
[d]Not calculated for this site.

TABLE B-V

COMPARISON OF ESTIMATED COSTS, VARIOUS REMEDIAL ACTIONS
VITRO SITE[a]

Option Number	Site-Specific Cost ($000)	Description of Remedial Action
I	36 400	Existing debris and rubble would be buried on site; the existing sewer line, access road, and drainage ditches would be rerouted over uncontaminated material; the pile would be reshaped and stabilized in place with 3 m of local earth cover. A riprap cover or natural vegetation would be provided. Off-site contaminated soil would be cleaned up.
I–P	41 010	Same as Option I except repiling and reshaping confined to 80 acres. Pile would be dewatered and covered with two inches of asphalt emulsion paving mixture, then further covered with two feet of gravel.
I–T	76 020	Same as Option I, except that tailings would be thermally stabilized before repiling. Covered with two feet of gravel.
II-A	82 500	The tailings, contaminated soil and rubble would be removed by rail to site 2, Natural Depression, 8 mi north of Clive, Utah, situated about 85 mi from the tailings site. The tailings site and off-site properties would be decontaminated and released for unlimited use.
IV	78 100	Same as Option IIA, except tailings removed to site 3, North Skull Valley, 2 mi west of Delle, Utah, located about 55 mi from the tailings site.

[a]Costs and descriptions of Options I, II-A, and IV taken from Tables 1 and 2 of Ford, Bacon & Davis Utah Inc. (1981).

b. Shiprock Site. In spite of a relatively high ratio of coal to tailings (0.146:1) required by the used rotary kiln equipment, the cost of thermal stabilization at Shiprock is lower than at any of the other sites (~$16.00 per ton). As shown in Table B-VI, this results in a project cost for thermal stabilization with disposal on site being less expensive than any moving option for a distance greater than five miles. The principal reason for this is the low price of coal for kiln operation in contrast to the high cost of diesel fuel for trucking. Another factor is the lower labor cost for kiln operations in contrast to the labor cost for radiological monitoring involved in site cleanup and tailings transportation. The costs in Table B-VI for simple in-place and remote disposal options were calculated by Ford, Bacon & Davis Utah Inc. for the 1981 Shiprock report.*

Two different production (conditioning) rate options were calculated for Shiprock, and the cost summaries are presented in Tables B-II and B-III. Table B-II shows the cost for the maximum projected rate possible with a single used rotary kiln, namely 500 ton/day. This table was prepared to show the comparison with Vitro site at the same rate. However, 500 ton/day would not complete remedial action within a 7-yr time limit, so an alternative plan using two kilns was developed that would process the pile in a little less than 5 yr. The 1000 ton/day system consists of two parallel process trains from kiln feed to stack, using only the coal crushing equipment and the feed and product belt conveyors in common. The total cost and the per ton cost of the 500 ton/day and 1000 ton/day options are negligibly different because the higher capital costs for 1000 ton/day operation (which have not been discounted nor assigned salvage value) are offset by lower labor and overhead costs.

TABLE B-VI

ESTIMATED COSTS OF VARIOUS REMEDIAL ACTION OPTIONS SHIPROCK SITE

Option	Location – Distance	Cost ($)
I	Cover with earth & riprap, in place	13 400 000
II	Many Devils Site – 4 mi.	25 600 000
III	Shiprock Campground – 6.8 mi.	29 000 000
IV	Rattlesnake Area – 8.3 mi.	27 400 000
V	Salt Creek Area – 8.5 mi.	30 100 000
I–T	Thermal stabilization plus 2 ft gravel, in place	27 216 000

*This information provided by R. D. Baird, Ford, Bacon & Davis Utah Inc., 1981.

c. Canonsburg Site. At the time of this analysis, the authors had been provided no written remedial action assessment reports on Canonsburg. The following comments are based on anecdotal information believed to be reliable.

A 300-ton/day thermal stabilization plant using the same labor budget and same cost of coal as the Vitro site was projected in calculating the costs in Table B-IV. Precise information on coal quality and costs has not been obtained, but the figure used in Table B-IV is on the high side. On the other hand, no allowance was made for the separation of "junk" in the pile from the tailings.

If we use the small plant contemplated, thermal stabilization of the 200 000 tons of tailings at Canonsburg could be completed in 2 years. If other on-site or off-site contaminated material is to be processed, the time may be a year longer and the cost 50% higher. Given the high level of environmental protection effort (special transportation equipment, stringent radiological monitoring) required for transportation and off-site disposal in a highly populated area, thermal stabilization may be the most attractive option for remedial action at Canonsburg.

d. Conclusions. A preliminary economic assessment of physicochemical tailings treatment alternatives reveals that thermal stabilization (sintering) is somewhat expensive but could be economically attractive at tailings sites where some or all of the following conditions prevail:

1. Coal for kiln operation is inexpensive.
2. Topsoil for cover is not readily available.
3. Transportation costs to remote disposal area are high.
4. Environmental (radiological) monitoring costs are high for transport to remote disposal area.

The Salt Lake City, Shiprock, and Canonsburg sites are believed to be economically attractive locations for thermal stabilization when compared with costs for remedial actions requiring relocation.

2. Conceptual Design of a Thermal Stabilization Operation

a. Summary. The entire process of thermal stabilization of a uranium mill tailings pile begins by establishing grades and levels in the existing pile, followed by excavation and some earth moving for compositing effect. The excavated material is conveyed by belt to a clod-breaker and drops into a feed silo, from which a screw conveyor carries it to the rotary kiln. From the kiln, the glassy clinker drops into a quench tank or is air-cooled, is conveyed to a product silo, and then passes, by belt conveyor, to the final disposal pile. Earth-moving equipment grades it into benches, the top bench (final pile grade) is covered with 2 ft of gravel (or other appropriate material).

b. Equipment. For 300 to 500 tons/day, only one small dozer, one grader, and a small (3 to 5 cubic yard) excavator are required. The dozer and grader can work both the feed (untreated tailings) and the product (sintered tailings) piles. For example, the outside crew could work the feed pile in the mornings, filling the feed silo, and then work the product pile in the afternoons, building the benches and emptying the product silo. The kiln equipment will operate 24 h/day. No trucks, other than a pickup for the superintendent, are required; all materials movement is to be by (movable) conveyors and earth-moving equipment, aside from coal and cover material trucked in by outside contractors.

c. Personnel. The functions of the personnel described in Table B-VII are obvious, aside from those of the superintendent. The compensation rates (wages plus benefits) are those estimated for Vitro and Canonsburg. A 10% reduction in the rates was made at Shiprock to reflect the lower prevailing wages in New Mexico (Table B-VIII).

Because of the relatively small scale of the operation, the superintendent can and should perform two functions: (1) site manager, which is essentially the operations manager for the site with the usual responsibilities, and (2) site engineer. In the latter capacity he would have the responsibility of laying out bounds, grades, levels, pitches, and benches in conformity with overall specifications prepared by the design engineers. The individual should preferably be a BS graduate in civil and mechanical technology, with several year's engineering and supervisory experience.

d. Capital Costs. Capital costs are shown in Table B-IX; all costs have been adjusted to March 1981. Cost for for air pollution control equipment, Item 6, was calculated according to Neveril (1980) for a venturi scrubber system plus heat recovery cooler, including stack. This particular estimate should be good at ±20%. Item 5 was estimated from the generalized cost data of Mills (1970) and has a likely error range of –20 to +40%. Part of this stems from the difficulty of estimating the required length of belt conveyor systems. The other capital costs are in the ±30% error range.

e. Operating Costs. The conceptual design of kiln operations was based on the cost of 11 300 Btu/lb coal delivered in Salt Lake City, as determined from various sources. This cost is based upon a gross heat requirement of 3 860 000 Btu per ton of feed and a design heat recovery of 22.5%. For Vitro site, the coal cost is good to ±5%. The coal cost for Shiprock was estimated from the known average Btu value of 10 200 Btu/lb at mine mouth and cost of $4.80 per ton plus a trucking charge (26 miles @ 0.18 per ton-mile), which yielded an estimated total of $9.48 per ton, delivered. Shiprock coal costs may be in error by –20 to +10%. Canonsburg coal costs were assumed to be the same (per Btu) as Salt Lake City. This error may be –30 to +10%.

Electricity costs were calculated from the respective unit cost figures indicated for maximum operating load of 400 hp. The connected load of the entire plant is approximately 500 hp, but only the stack fan (100 hp) and the kiln rotators (150 hp) will be operating all the time.

Labor costs were estimated using input on Salt Lake City wages.* The error is estimated at ±15%.

Miscellaneous operating costs include maintenance parts, rental/depreciation of earth-moving equipment, water (50 to 60 gpm), and the cost of obtaining and placing 2 ft of gravel cover on the contoured pile of stabilized material. These were estimated by the authors from data obtained from various sources and may be in error by –10 to +30%.

Wind-blown and off-site remedial action costs for Vitro site were obtained from Ford, Bacon & Davis Utah Inc. (1981).

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*This information provided by R. D. Baird, Ford, Bacon & Davis Utah Inc, 1981.

TABLE B-VII

PERSONNEL AND COMPENSATION VITRO SITE—500 TON/DAY

Number	Job Title	Compensation[a] ($/hr)
(Employees on day shift only)		
1	Superintendent	25.00
1	Foreman and Heavy-Equipment Operator	18.00
1	Heavy-Equipment Operator	17.00
2	Laborers, Helpers, etc.	11.00
1	Health Physics Professional (Technical Supervisor)	25.00
1	Health Physics Technician	15.60
(Employees on each of three process-plant operating shifts)		
1	Foreman and Chief Plant Operator	18.00
1	Assistant Plant Operator	17.00
1	Maintenance Technician	17.00
1	Oiler, Helper	11.00
1	Security Guard	10.00

TABLE B-VIII

PERSONNEL AND COMPENSATION SHIPROCK SITE—1000 TON/DAY

Number	Job Title	Compensation[a] ($/hr)
(Employees on day shift only)		
1	Superintendent	22.50
1	Foreman and Heavy-Equipment Operator	16.20
3	Heavy-Equipment Operators	15.30
2	Laborers, Helpers, etc.	9.90
1	Technical Supervisor	22.50
2	Health Physics Technicians	14.05
(Employees on each of three process-plant operating shifts)		
1	Plant Foreman	16.20
2	Kiln Operators	15.30
1	Maintenance Technician	15.30
1	Maintenance & Operations Helper	11.50
1	Oiler & Helper	9.90
1	Security Guard	9.00

[a]Compensation includes direct wages/salaries plus value of benefits and is based on January 1981, Salt Lake City prevailing wages.

TABLE B-IX

SUMMARY OF CAPITAL COSTS FOR 500 TON/DAY[a] THERMAL STABILIZATION (SINTERING) PLANT

1.	Purchase of used 2300°F kiln, as is	$ 400 000[b]
2.	Dismantling and shipping	150 000
3.	Site preparation, foundations, installation of kiln & auxiliaries, engr. & contractors' fees	1 500 000
4.	Coal pulverizer & handling equipt., installed	500 000
5.	Storage silos, lump-breaker, quench tank, and conveyors—installed	700 000
6.	Stack gas dust removal equipment – installed	500 000
7.	Total	$ 3 750 000

[a]Heat rate of conceptual design is 1 340 000 Btu/min or approximately 3 860 000 Btu/ton of feed. Gas rate is 15 120 scf/min; 22.5% heat recovery is contemplated.
[b]Chem-Oil Corp. provided estimate of $250 000 for a 300 ton/day used unit. The unit contemplated (an inclined rotary kiln) would be 8 to 12 ft in diam and 360 ft in length.

3. Energy Consumption for Shiprock Remedial Action Alternatives

Using energy-inefficient, early-model rotary kiln technology for the plant and process described in the previous section, the estimated total coal consumption at Shiprock is 249 200 tons or 536×10^{10} kJ of fossil fuel energy. In terms of energy consumption alone, the thermal stabilization option is far less attractive than any of the earth-moving alternatives, whose energy costs range from 4.45×10^{10} kJ for covering in place through 13.9×10^{10} kJ at the Salt Creek and Oil Field sites to a high of 21.5×10^{10} kJ at the strip mine site. About the only encouraging energy comparison that can be made between thermal stabilization and the earth-moving alternatives is that only 4.6×10^{10} kJ of diesel fuel will be needed in connection with the thermal stabilization option (this includes fuel for trucks hauling coal from the mine), which is about the same as the least expensive earth-moving option. If the conservation of liquid fuel for transportation is essential, then thermal stabilization is clearly better than most of the remote disposal options since their entire energy consumption is liquid fuel.

The detailed energy budget for thermal stabilization at Shiprock is presented in Table B-X. All entries are in units of 10^{10} kJ. The first column presents the estimated consumption of energy for the given item as directly converted from its engineering unit of measurement to kilojoules (a kilojoule is 0.948 Btu). The second column, in which only the electricity value is changed, allows for the inefficiency of conversion of fossil fuel to electrical energy. The third column allows for the relative economic value of electricity and of coal compared with liquid (diesel) fuel. Diesel fuel costs only slightly less than electricity (in the Shiprock area), whereas it costs 34 times as much as coal on a unit of energy basis. The adjusted "economic-energy-equivalent" bottom line of the third column explains in large degree why the dollar costs of thermal stabilization are less than those for moving the pile more than 5 miles. February 1981 prices were used in the Shiprock area: electricity $0.04/kWh; diesel fuel $1.25/gal.; coal (at pithead) $4.80/ton.

4. Municipal Waste Codisposal Options and Economics

a. Purpose of Codisposal of Tailings with Municipal Waste. Codisposal of tailings with municipal waste would be feasible only in a locality with a fairly large population near the tailings site. Salt Lake City fits this description; Canonsburg may fit the necessary conditions also. Codisposal would be feasible because the combustion of municipal waste would supply heat for the thermal stabilization process, given certain favorable conditions. The other potentially attractive factor is that some air pollution control equipment could be shared by the two facilities and remain available to the municipal

TABLE B-X

ENERGY COSTS OF THERMAL STABILIZATION AT SHIPROCK SITE, 10^{10} kJ

Item	Energy Consumption (10^{10} kJ) Estimated Actual	Fossil Fuel Equivalent	Diesel Fuel kJ/$ Equivalent
Kiln Fuel (249 200 ton coal)[a]	536.0	536.0	15.7
Electric Power (2.434×10^7 kWh)	8.76	29.2	11.86
Excavate & Load Tailings (105 000 gal. of Diesel Fuel)	1.6	1.6	1.6
Excavate & Haul Cover (20 700 gal.)	0.315	0.315	0.315
Grade Tailings & Cover (37 100 gal.)	0.565	0.565	0.565
Haul Coal from Mine to Plant (138 600 gal.)	2.11	2.11	2.11
Total (Rounded)[b]	549.0	570.0	32.2

[a]10 200 Btu/lb.
[b]Totals do not exactly equal sum of entries because of rounding of all entries.

waste facility after completion of remedial action on the tailings. Some capital cost savings during construction might also be possible. In this study, two possibilities were considered: (1) codisposal in a single unit and (2) use of coupled, but independent, units for the two different purposes.

b. Commercially Available Municipal Waste Processes. A great many different processes for the combustion of municipal waste have been proposed and tried on, at least, a pilot or semiworks scale. Relatively few processes have a significant number of US installations with operations extending over a period of five years or more. Seven different types are listed, three of which have a significant record of performance. They are

(1) Waterwall refuse boiler (e.g., Wheelabrator-Frye Process)

This type of incinerator usually has a traveling grate or an inclined shaking grate. The combustion heat of the refuse is transferred to the water in the (tube) walls, generating steam of moderately high pressure. Slagging must be avoided to prevent clogging of the grates.

(2) Nonslagging shaft kiln with secondary combustion boiler (e.g., Monsanto Landgard Process)

Municipal waste is burned with air in a shaft kiln with slight deficiency of air and at a moderate temperature to avoid slagging. The exit gas is hot and contains about 100 Btu/scf. This gas is burned in a separate boiler to produce steam.

(3) Slagging shaft kiln with secondary combustion chamber (e.g., Andco-Torrax Process)

In this process the kiln is designed much like a blast furnace with air injected through tuyeres for combustion of the refuse, while still producing a low-Btu hot gas for secondary combustion in an adjacent boiler.

(4) Slagging shaft kiln using oxygen for combustion (e.g., Purox Process)

The kiln design is also similar to a blast furnace, but oxygen introduced through the tuyeres permits complete combustion of the waste and produces a gas, which is of low temperature and in the medium-Btu heat content range. The gas is sold to a nearby customer.

(5) Down-draft slagging incinerator

This unique design solves the nagging problem of slag erosion of refractory by introducing the feed around the periphery of a cylindrical vessel with a conical bottom. A downward-directed flame of oil or gas is injected at the top center. The exterior walls of the vessel are sufficiently cool so that, after start-up, cooled slag forms its own refractory lining. Use of this device obviously requires sufficient slagging material in the feed. Reasonable uniformity of size distribution and possibly a rather narrow range of size distribution of the feed may be needed. Energy recovery is from heat transfer from the gases only.

(6) Two-stage, ram-actuated continuous step grate system (e.g., Consumat Systems, Inc.)

In this system the waste is fed from hoppers onto a series of stepped grates in the refractory-lined primary combustion chamber. Rams force the burning and burned material along the grates, not through them. The air/fuel ratio is insufficient for complete combustion of the vaporized/pyrolyzed substances but is sufficient to retain only a small amount of char (2 to 3%) in the solid waste. The hot, incompletely burned gases then pass on to a second chamber where combustion is completed and finally go to a heat exchanger where energy is extracted from the gases to produce high-pressure steam.

(7) Two-stage, pulsed (stepped) hearth waterwall batch systems (e.g., Basic Environmental Engineering, Inc.)

This system combines some of the advantages of waterwall primary combustion chamber construction with the ability of a secondary combustion chamber to destroy residual organics in the gases, followed by more heat recovery from steam production. The batch designation does not refer to feeding but rather to ash removal, which needs to be performed only infrequently.

These seven types do not exhaust the possible variations but represent as wide a range as is necessary for the purpose of this report. Selection of these seven does not constitute either endorsement or unfavorable criticism of any other commercial product for general waste disposal applications.

c. Compatibility of Commercially Available Processes with the Thermal Stabilization Process. Because none of the above seven processes would work on tailings alone, it would be necessary to mix coal (or coke) with pelletized tailings and use this mixture as a feed to the unit. The three horizontal units (Processes #1, #6, and #7 described in the previous section) do not operate at a sufficiently high temperature to meet thermal conditioning/sintering objectives. The three shaft-kiln or blast furnace types (Processes #2, #3, and #4) would be subject to bridging or clogging except at unacceptably high coal/tailings ratios. The down-draft combustor (Process #5) would not require much coal with the tailings but would have an overall unacceptably high fuel consumption.

To utilize the fuel value of the refuse, one must ask what mixture of tailings to waste is needed to *simultaneously* dispose of both. After eliminating the horizontal units (#1, #6, and #7) because of inadequate operating temperatures, we can predict a possibly practical ratio at 0.46 lb of average municipal waste per pound of tailings. However, this ratio of waste to tailings is, in our opinion, really a lower limit, which is not likely to be attainable in a vertical unit. A mass ratio of waste to tailings of 1:1 or higher is likely to be necessary to avoid the bridging/plugging problems mentioned above. If 1:1 ratio did work satisfactorily, one is then faced with 20% more ash material (which must be considered as some sort of low-level radioactive waste) than the original tailings. This is not a highly desirable result.

Finally, the question is what will the presence of municipal waste ash do to the characteristics of the TST "clinker." The answer is that we simply do not know. In general, we assume that the glass in the waste will have a beneficial effect, but PVC plastics, etc., could be harmful. There is no way of knowing without testing.

There remains the possibility of combining a municipal waste disposal system with the thermal stabilization process in *two* stages producing *separate* municipal waste ash (nonradioactive) and TST clinker. The municipal waste ash could actually be usable as a gamma attenuation cover for the TST "clinker" product. It is assumed that, by close coupling of the two processes, hot gases from the municipal waste process could be burned in the rotary kiln for TST process, in place of the projected use of a pulverized coal burner. (Supplementary fuel would probably be required in the kiln, at least for start-ups.)

Examination of the details of the various technologies where possible (details were not available on Process #1) shows that this is likely to be technologically feasible only with Process #4 (Purox) or Process #6 (Consumat). There are practical objections to each of these two processes.

There is no real technical problem with the off-gas from the Purox process. It is really a very good medium Btu gas, averaging 350 Btu/scf. It would be a satisfactory fuel for a thermal stabilization kiln. However, the economic value of the gas is about 50% greater (at Salt Lake City) than the estimated energy equivalent amount of powdered coal. If the municipal waste disposal facility were considering Purox (which is a rather expensive process and not widely installed), it would not be eager to subsidize the thermal stabilization process, despite some potential advantages of joint operation.

There are both technical and engineering problems with the off-gas from the first stage of the Consumat process. First, the modular design of the Consumat units would have to be radically altered to permit alternative coupling to the lower end of a rotary kiln. It might not be feasible at all. Second, the operating conditions would have to be altered in the primary combustion chamber to produce a 150 to 170 Btu/scf gas at about 600 to 750°C. There is grave doubt that this could be done without raising the char (unburned carbon) in the ash from the primary combustor to economically unacceptable levels. There is considerable doubt that Consumat would be willing to change their design themselves (for a fee) or permit anyone else to do it, for fear of damage to their reputation for building and installing successful and economically desirable units. Thus it appears that two-stage codisposal is a potentially viable alternative for which no commercially available first (municipal waste) stage may be available at the present time.

d. Summary of Engineering and Economic Considerations—Codisposal. In summary of the preceding discussions, Table B-XI lists the major advantages and disadvantages of combining the thermal stabilization process with municipal waste disposal. This, of course, assumes that the tailings pile is located in a sufficiently populous area to make municipal incineration for energy recovery attractive as an alternative to landfill.

Table B-XII summarizes a number of characteristics of a possible *two-stage* codisposal process, many of which have not been discussed in this report but appear largely self-explanatory. It should be commented that the salable energy output of a stand-alone municipal waste plant is either steam for manufacturing/heating use or electricity from a steam-driven turbine. It is assumed in Table B-XII that Salt Lake City conditions will apply and that electricity will be the salable energy. It is also assumed that the high engineering expenses mentioned would apply to the design of a modified Consumat-type primary combustor with switchable coupling either to a secondary combustion chamber-boiler or to the thermal stabilization kiln.

The final result of this analysis is that the use of municipal waste to fuel a thermal stablization facility is probably technically feasible but that disadvantages outweigh benefits, making codisposal an unattractive scheme. A coal-fired rotary cement kiln appears to be the most favorable technology to apply to the thermal conditioning of tailings.

TABLE B-XI

THERMAL STABILIZATION OF TAILINGS: CODISPOSAL WITH MUNICIPAL WASTE

ADVANTAGES

- Two different waste problems solved at once.
- Potential reduction in capital spending required.
- Enhanced size of waste facility to accommodate future municipal growth.
- Saving of fossil fuel by substitution of waste material.

DISADVANTAGES

- Single-stage codisposal limited in tailings-waste ratio.
- Auxiliary fossil fuel still required for maximum TST temperature.
- Unknown effect of waste admixture on quality of TST clinker.

TABLE B-XII

THERMAL STABILIZATION OF TAILINGS: TWO-STAGE CODISPOSAL PROCESS

ADVANTAGES

- Units can be decoupled yet use same air pollution control system.
- If waste unit shuts down, tailings kiln will run on full auxiliary fuel (i.e., coal).
- If kiln shuts down, waste unit will operate steam-electric generator.
- Ash from Unit I (waste incinerator) can serve as gamma cover for clinkers from Unit II (kiln).
- When tailings are all processed, Unit I is stand-alone electric generator.
- Some cost savings in combined initial construction should be possible.

DISADVANTAGES

- Value of fuel gas creditable to operations is no cheaper than using coal (at SLC).
- Engineering expenses may be high.

APPENDIX C

PRODUCTION AND EVALUATION OF THERMALLY STABILIZED TAILINGS PRODUCED IN A BATCH ROTARY FURNACE

1. Thermal Treatment Procedure

Thermal stabilization tests were performed at the U.S. Smelting Furnace Company in Belleville, Illinois using their No. 2 (1-ft^3) US Rotary Furnace. The tests were run over a one-week period. Salt Lake City tailings, as described in Sec. IV.A, were used. Operation conditions and observations are reported in Tables C-I and C-II, respectively. Figures C-1 through C-8 show photographs of the input materials and various sintered tailings. Figures C-9 through C-11 show photomicrographs of thin sections from individual heat-treated agglomerates.

2. Elemental Loss and Enrichment

Major nonvolatile elements, such as Al and Na, provide a means of determining sample weight loss (see Table C-III). Some volatilized elements (corrected for sample weight loss) and the degree of volatilization are given in Tables C-IV and C-V.

3. Reduction in Radon

The emanating ^{226}Ra values and reduction levels for many of the thermally stabilized tailings are given in Table C-VI. The response of emanating ^{226}Ra to leaching is presented in Table C-VII.

4. Column Leaching Procedure

Approximately 130 g of untreated or thermally stabilized tailings were placed in a column with a glass frit bottom. The leachate line was clamped to maintain immersion of the tailings in water; the initial sample wetting for each column used 153 mℓ of deionized water to immerse the sample with the least bulk density and maintain a constant liquid/solid ratio among columns. The initial water immersion lasted one day; then, the column was drained and the leachate filtered with 0.45-μm micropore filters. The pH, conductivity, Eh, and volume of the leachate from each column were measured immediately. The column was refilled with a volume of deionized water equivalent to the leachate volume drained from that column. Ten successive leaches were performed on each column; the fifth and tenth leaches were in contact for three days (over the weekend) rather than one day. The solids were dried after the tenth leach and measured for radon emanation (see Table C-VII). The leachates were analyzed by ion chromatography for SO_4^{-2}, Cl^-, and F^-, and by DC plasma emission spectroscopy for a number of major, minor, and trace constituents (see Table C-VIII).

TABLE C-I

PARAMETERS FOR THERMAL STABILIZATION TEST RUNS

Test Run No.	Date	Charge Start Time	Input Type	Input (kg)	Treatment Temp (°C)	Heat-up Time (min)	Treatment Time (min)	Quench Type: Air Cooled Ingot	Quench Type: Air Cooled Pan	Quench Type: Water	Furnace Operation Mode[a]
1	4/12	8:45	Sand	23	1400	–	–	–	–	–	–
2	4/12	11:45	AVG	23	1150	10	5		√[b]		Std
3 A–I	4/12	14:15	AVG	23	1000	20	15	A	B	C	Std
3							35	D	E	F	
							65	G	H	I	
4	4/13	8:30			1050	–	–		√[b]		Std
5	4/13	9:00	AVG	2.3	1050	3	15	√			Std
6	4/13	9:24	AVG	2.3	1050	5	30	√			Std
7	4/13	10:10	AVG	2.3	1050	5	60	√			Std
8	4/13	12:13	AVG	2.3	1050	3	15		√		Std
9	4/13	12:35	AVG	2.3	1050	6	15		√		Std
10	4/13	13:03	AVG	2.3	1050	3	12			√	Std
11	4/13	13:36	AVG	2.3	1100	3.5	8.5	√			Std
12	4/13	13:52	AVG	2.3	1100	3.5	2.5	√			Std
13	4/13	14:17	AVG	2.3	1100	3	2.5			√	Std
14	4/13	14:41	AVG	2.3	1100	4	2.5		√		Std
15	4/13	15:29	AVG	2.3	1075	3	5		√		Std
16	4/14	8:50	LARGE	4.5	1075	5	5.5		√		Std
17	4/14	9:23	LARGE	4.5	1050	4	15		√		Std
18	4/14	9:51	MIX	4.5	1050	4	5		√		Std
19	4/14	10:17	MIX	4.5	1050	5	5		√		Auto
20	4/14	10:45	MIX	4.5	1100	5	16		√		Std
21 A	4/14	11:35	AVG	4.5	1075	4	3		√		Auto
21 A–L[c]		14:47		each run		each run	each run		each run		
22	4/14	15:00	COAL	4.5	1000	5	15		√		Std
23	4/14	15:28	COAL	4.5	1050	5	15		√		Std
24	4/15	8:09	COAL	4.5	1075	4.5	15		√		Std
25	4/15	8:38	COAL	4.5	1075	5	15	A		B	Std
26	4/15	9:09	COAL	4.5	1075	5	28		A		
							60	B	C	D	Std
27	4/15	10:27	COAL	4.5	1100	5	15	A	B	C	Std
28	4/15	11:00	COAL	4.5	1100	5	30	A	B	C	Std
29	4/15	11:50	COAL	23	1100	7	60	A	B	C	Std
30	4/15	1:10	90% AVG 10% Pulver Coal	4.5	1100	5	15		√		Std
31	4/15	1:35	NaOH	4.5	1100	5	15		√		Std
32	4/15	2:00	Furnace Residue	–	1525	–	60	A		B	Auto to 1375°, O_2 assisted to 1525°
33	4/15	3:16	Borax	4.5	1525	–	30	√			Auto, O_2 assisted
34	4/15	4:05	Sand Na_2CO_3	9.1 4.5	1375	–	45	–	–	–	–

[a]Std — Manual flame control until treatment temperature reached, then automatic control. (This procedure was less violent than turning to automatic initially, which would open the flame to full blast.)

[b]Spoon used to remove viscous material from furnace.

[c]12 replicate runs.

TABLE C-II

OBSERVATIONS MADE DURING THERMAL STABILIZATION TEST RUNS

Test Run

1 Residual material from previous uses removed by melting sand. U. S. Smelting Furnace Company indicated that a lead-tin dross was the last material in the furnace (probably contained Si, Na, Pb, and Sn).

2 The tailings agglomerates popped and crackled as residual water was vaporized. Significant off-gassing occurred—possible HCl, Cl_2, or SO_2; off-gassing occurred with all test runs on these tailings at temperatures below 1000°C but was most pronounced at 1000 to 1200°C. The tailings charge formed a 15-cm-diam roll as long as the furnace, which could not be discharged; the sample was removed using a metal spoon. Then the furnace was heated to 1400°C, making a viscous product, which was pulled from the 12-cm discharge orifice.

3 The sample did not appear sintered; off-gassing was still occurring after one hour treatment. The angle of repose of the material bed was ~45°.

4 A few pieces of material from test run #3 remained in the furnace and were well sintered and slightly fused; it appeared that a thin bed, cool walls, and hot flame were the best operating conditions.

5 Angle of repose for the ~2.5-cm-thick bed was about 60°. A uniformly heated bed was attained in ~3 min; the flame ran hot the full treatment time. The surface of the sample appeared much hotter (whiter) than the furnace walls. About one-half of the sample mass adhered to the walls.

6 Furnace flame idled most of the treatment time and sample did not appear as hot as in test run #5. Most of the sample poured out easily upon discharge.

7 After the initial 5-min heatup, the flame was on full blast for two 5-min periods and one 12-min period. Less material was discharged than for test run #5.

8 Flame at idle after 3-min heatup and intermittently thereafter.

#12 Flame went to idle one-half min before sample was dumped.

#13 Output material was very viscous.

#14 Agglomerates started sticking together after 1 min at temperature. Output material very viscous.

#15 Raised temperature to 1400°C after sample was dumped to smooth out the furnace lining.

#16 Agglomerates barely stuck to furnace wall when treatment temperature reached. Considerable sticking was noted at discharge time. Typical deviations in wall temperature appear to be ±15°C.

#17 LARGE material not as well sintered as AVG under similar conditions.

#18 Flame idle after 8 min.

TABLE C-II (cont)

#19 Flame idle after 5 min.

#20 Sample (MIX) formed roll in 6 min; roll broken with rod; balls formed. Material in furnace was less plastic and sticking less than AVG material. The flame was on full most of the treatment time.

#21A-#21L A series of 12 runs to produce 45 kg of the apparent best sintered AVG material with the discharge being discrete agglomerates. The procedure was to heat the material under full flame (Auto) 4-min heatup and 3-min treatment. Then the flame was idled, and any large masses of material were broken up before dumping Generally, no large clump was formed.

#22 A great deal of dark orange flame exited from the flame inlet hole during heating of COAL material. Sample was not sticky; however, it contained some material from previous runs.

#23 Flame same as #22; took about 5 min to consume the coal and return flame to normal appearance.

#24 Smoky flame for 3 min. Some sticking to walls as discrete agglomerates. The COAL samples appear more time dependent than the AVG material, which was primarily temperature dependent.

#25 Smoky flame for 2.5 min.

#26 Agglomerates stuck to each other and to the furnace wall but did not form large chunks (>8 cm).

#27 Agglomerates formed small (2-5-cm) balls. A great deal of sticking to the wall was noted. As expected, the air quench in the ingot molds retained their heat longer than open air-cooled (pan-quenched) samples.

#29 Smoky orange flame disappeared after 7 min. Much of the sample stuck to the walls. Small samples were obtained for ingot, pan, and water quenches.

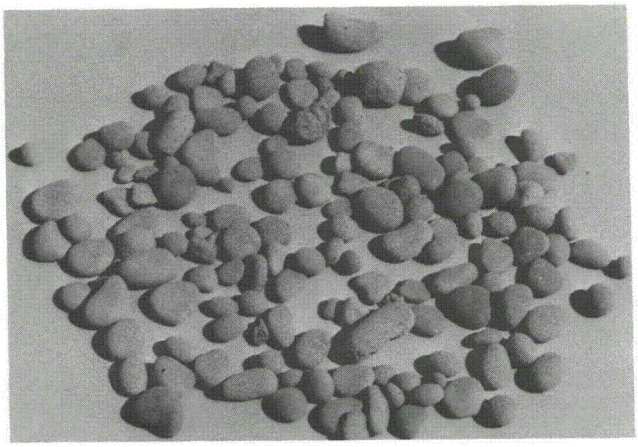
#30 Sample behaved more like AVG material than COAL material, i.e., more slagging. Smoky flame from pulverized coal combustion.

#31 Very viscous slag produced; walls of furnace had to be scraped to obtain several hundred grams of product.

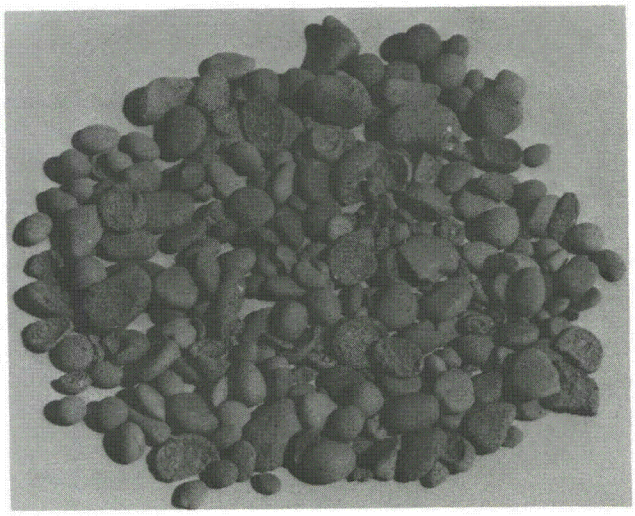
#32 Walls began to drip molten slag at 1260°C; viscous fluid formed at 1370°C. Glassy slag was poured into 4 ingot molds and some were water-quenched.

#33 Borax "wash" used to remove residual materials as fluid glass.

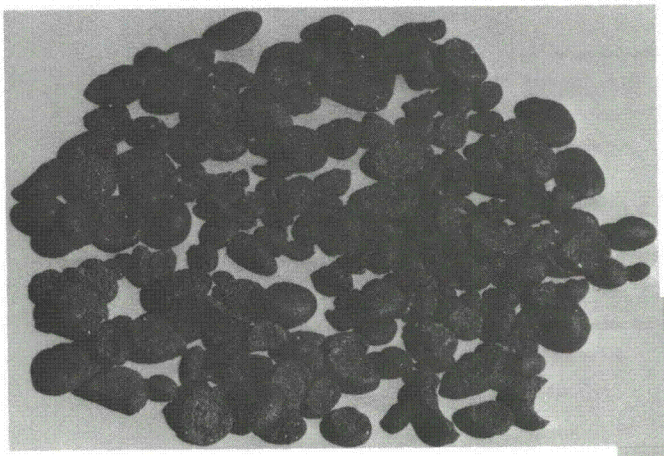
#34 Sand/soda mixture formed flowing glass, which produced a smooth glass lining on the furnace.



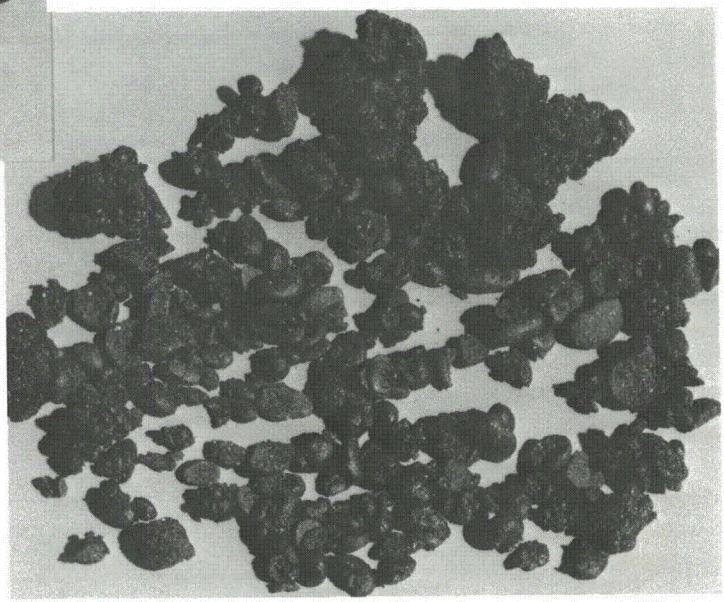
a. Additive: none.
0°C.
0 min.



b. Run # 3E.
Additive: none.
1000°C.
35 min.
Pan quench.



c. Run #8.
Additive: none.
1050°C.
15 min.
Pan quench.



d. Run # 15.
Additive: none.
1075°C.
5 min.
Pan quench.

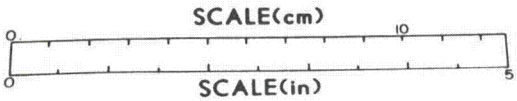
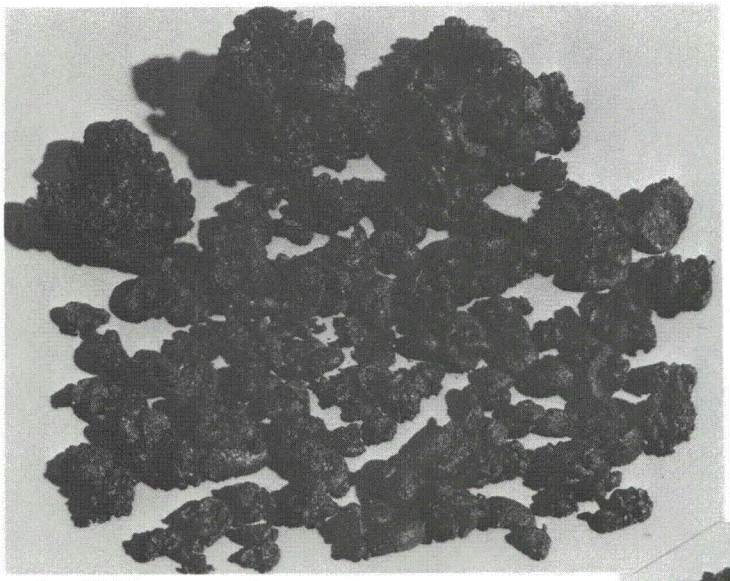
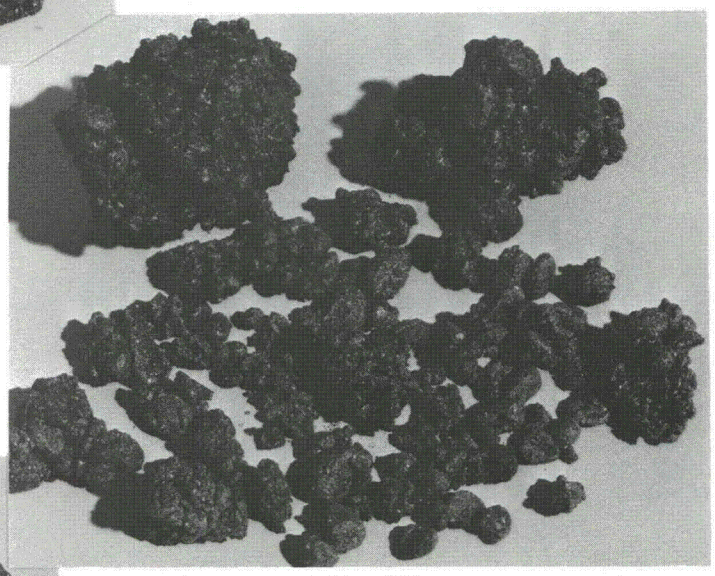


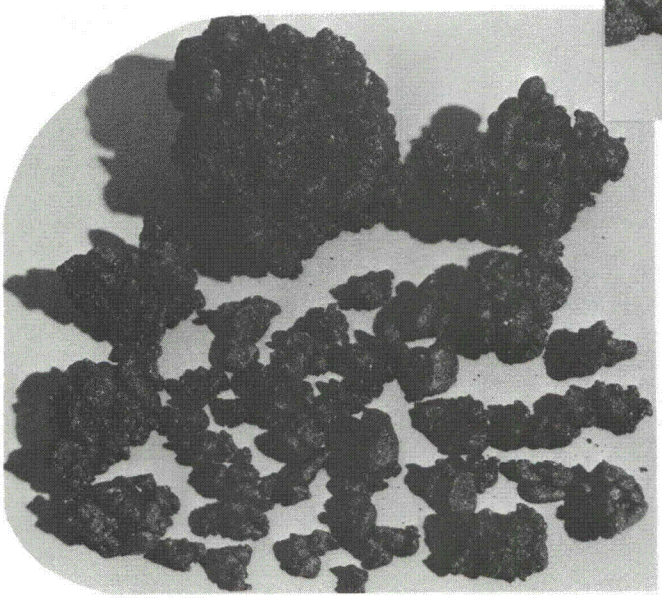
Fig. C-1. Untreated and thermally stabilized Salt Lake City tailings—AVG material (see Sec. IV of text for description).



a. Run # 12.
Additive: none.
1100°C.
2.5 min.
Ingot quench.



b. Run # 13.
Additive: none.
1100°C.
2.5 min.
Water quench.



c. Run # 14.
Additive: none.
1100°C.
2.5 min.
Pan quench.

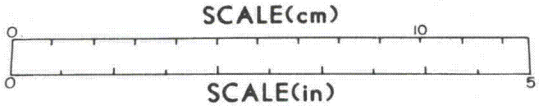
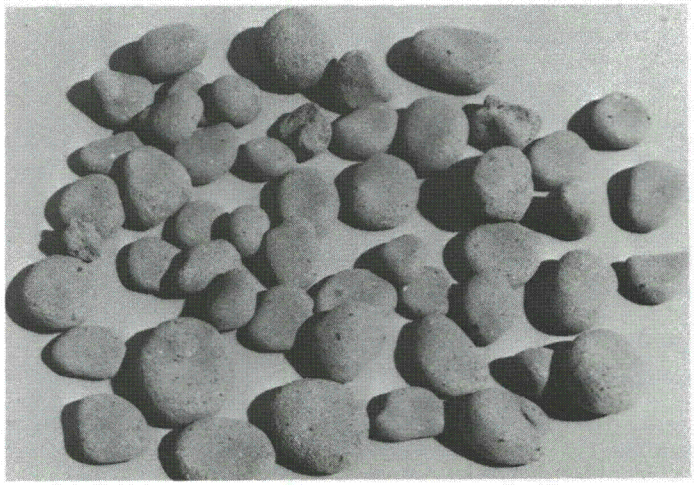
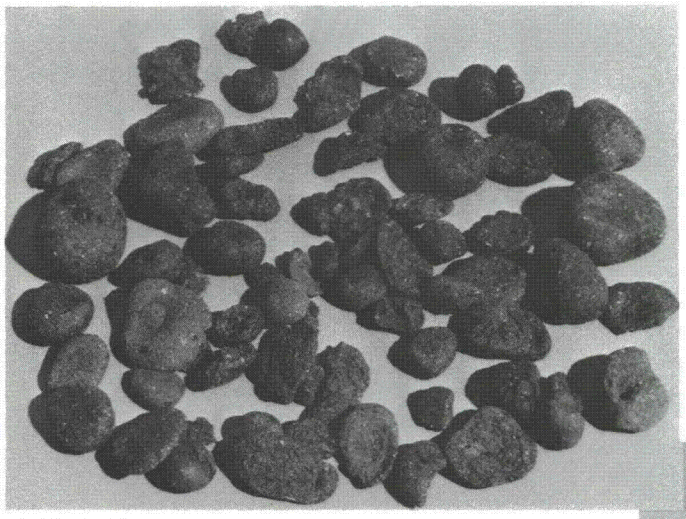


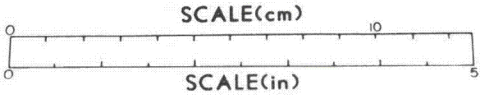
Fig. C-2. Thermally stabilized AVG material (1100°C)—different types of quenching.

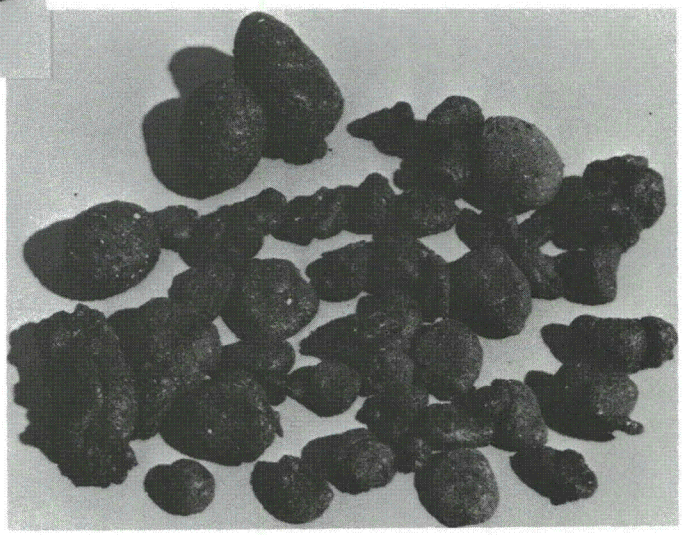


a. Additive: none.
0°C.
0 min.



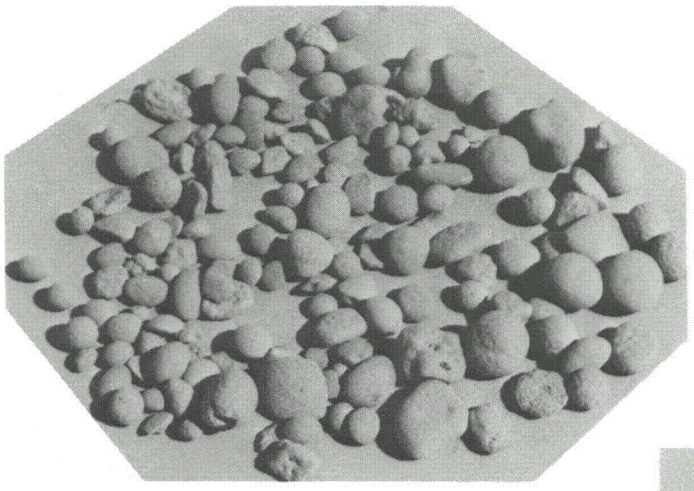
b. Run #17.
Additive: none.
1050°C.
15 min.
Pan quench.



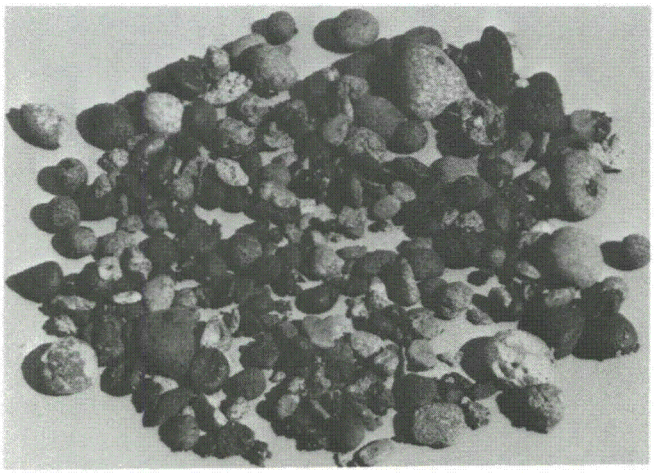


c. Run #16.
Additive: none.
1075°C.
5.5 min.
Pan quench.

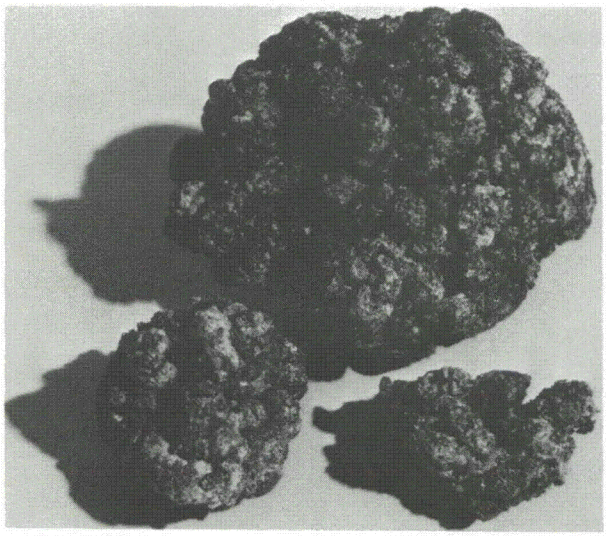
Fig. C-3. Untreated and thermally stabilized Salt Lake City tailings—LARGE material.



a. Additive: none.
0°C.
0 min.



b. Run # 19.
Additive: none.
1050°C.
5 min.
Pan quench.



c. Run # 20.
Additive: none.
1100°C.
16 min.
Pan quench.

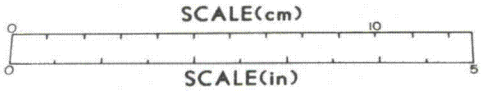


Fig. C-4. Untreated and thermally stabilized Salt Lake City tailings—MIX material.

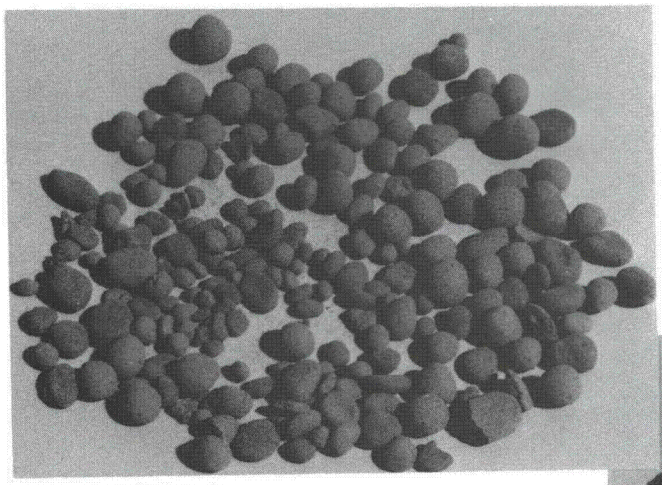
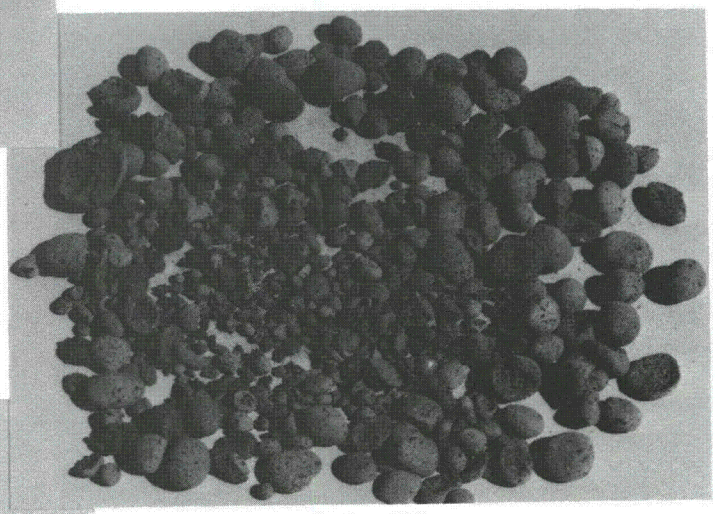
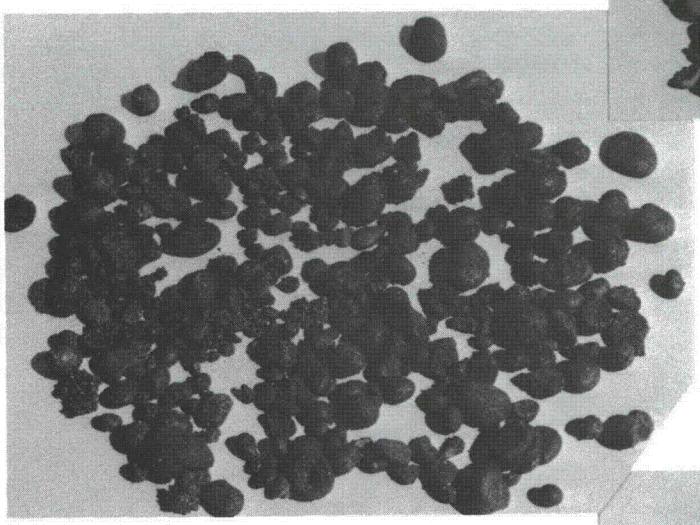


Fig. C-5. Untreated and thermally stabilized Salt Lake City tailings—COAL material.

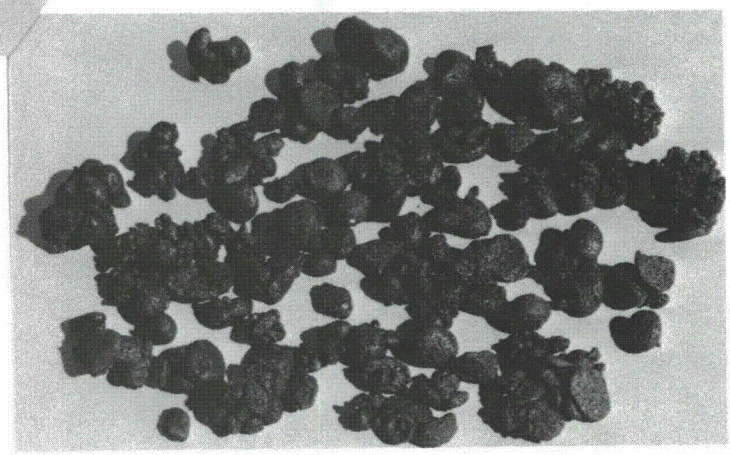
a. Additive: 10% coal.
0°C.
0 min.



b. Run #22.
Additive: 10% coal.
1000°C.
15 min.
Pan quench.



c. Run # 23.
Additive: 10% coal.
1050°C.
15 min.
Pan quench.



d. Run #24.
Additive: 10% coal.
1075°C
15 min.
Pan quench.

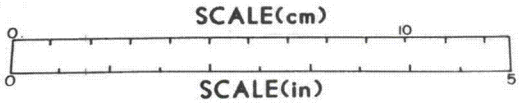
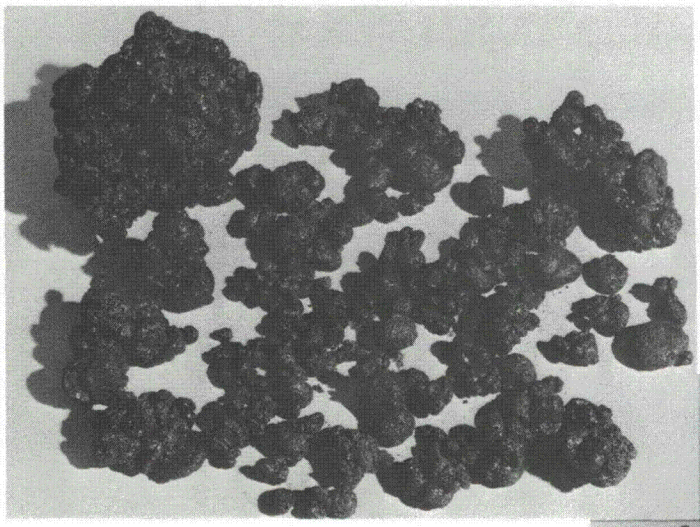
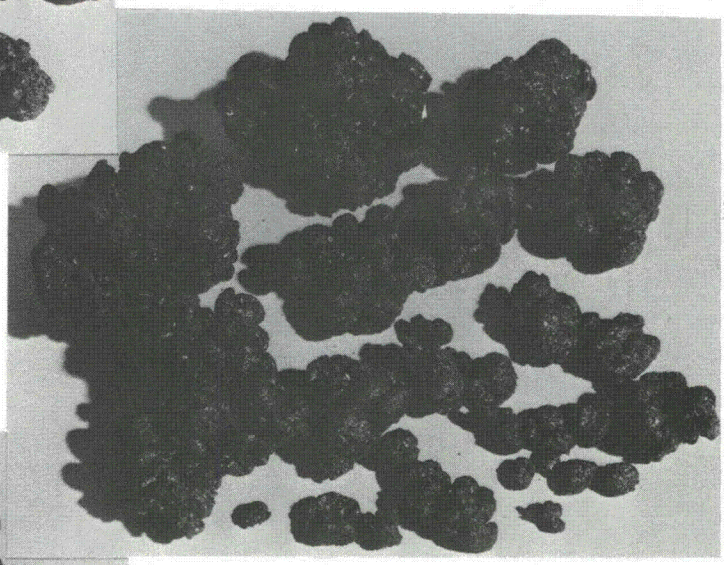


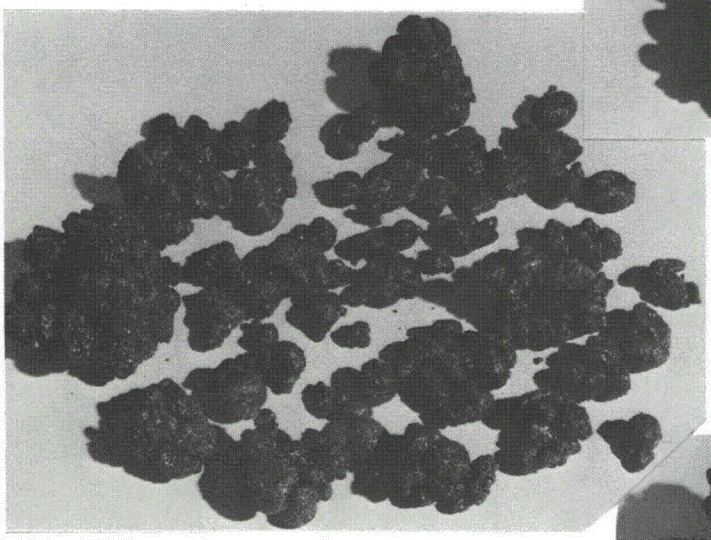
Fig. C-6. Thermally stabilized COAL material (1100°C)—different treatment times and quench types.



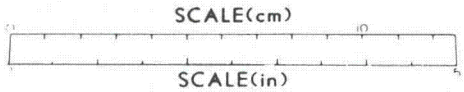
a. Run #27A.
Additive: 10% coal.
1100°C.
15 min.
Ingot quench.

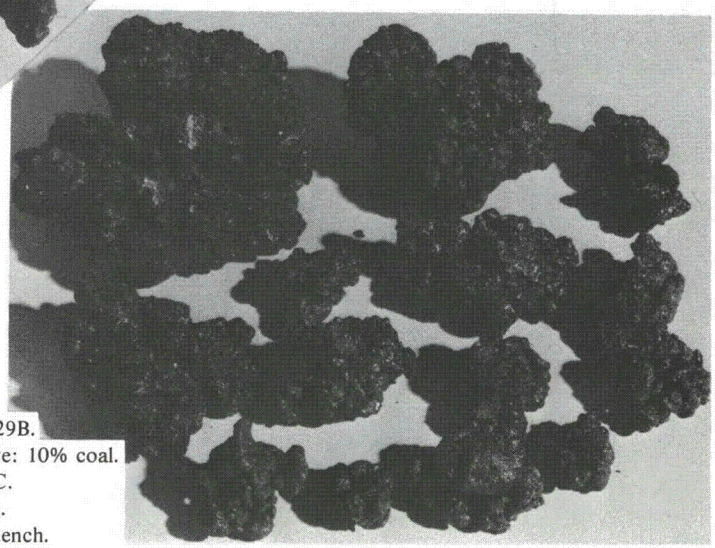


b. Run #28B.
Additive: 10% coal.
1100°C.
30 min.
Pan quench.



c. Run #28C.
Additive: 10% coal.
1100°C.
30 min. Water quench.





d. Run #29B.
Additive: 10% coal.
1100°C.
60 min.
Pan quench.

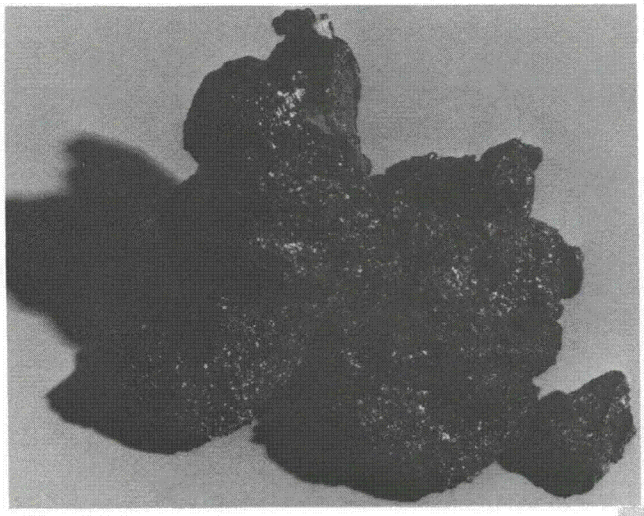
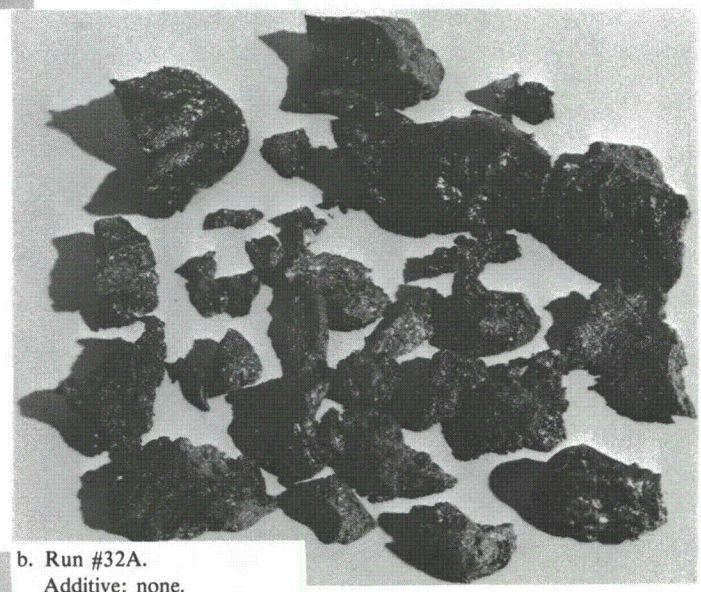
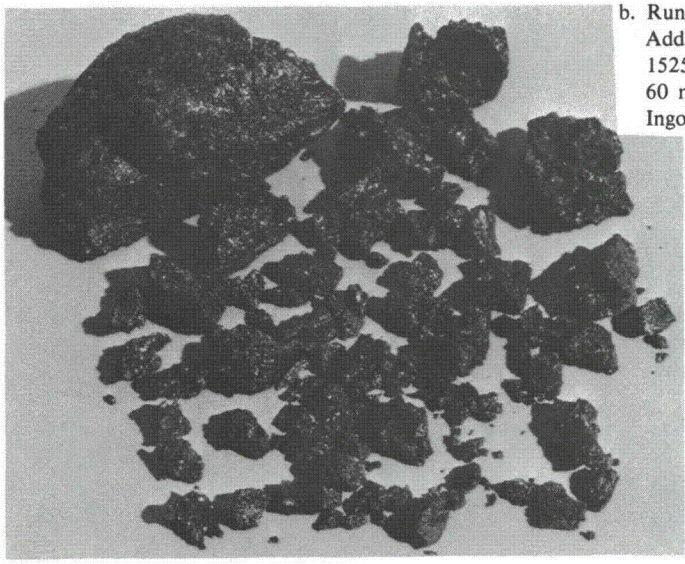


Fig. C-7. Vitrified Salt Lake City tailings (1450 and 1525°C).

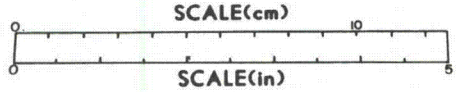
a. Run #2b.
Additive: none.
1450°C.
60 min.
Pan quench.

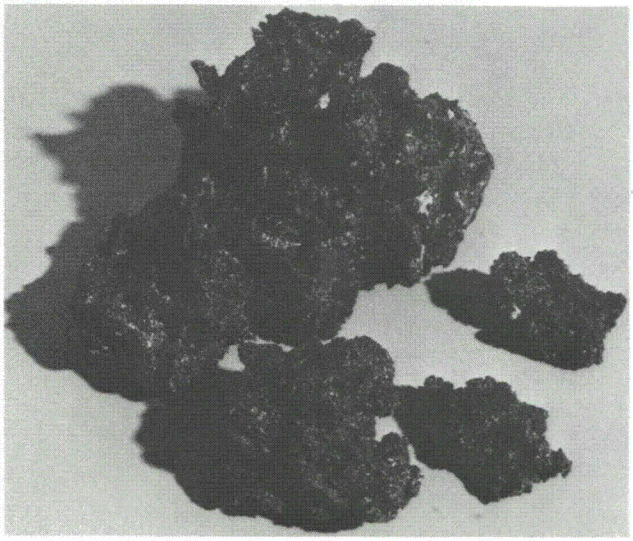


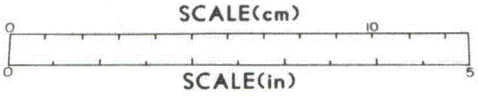
b. Run #32A.
Additive: none.
1525°C.
60 min.
Ingot quench.



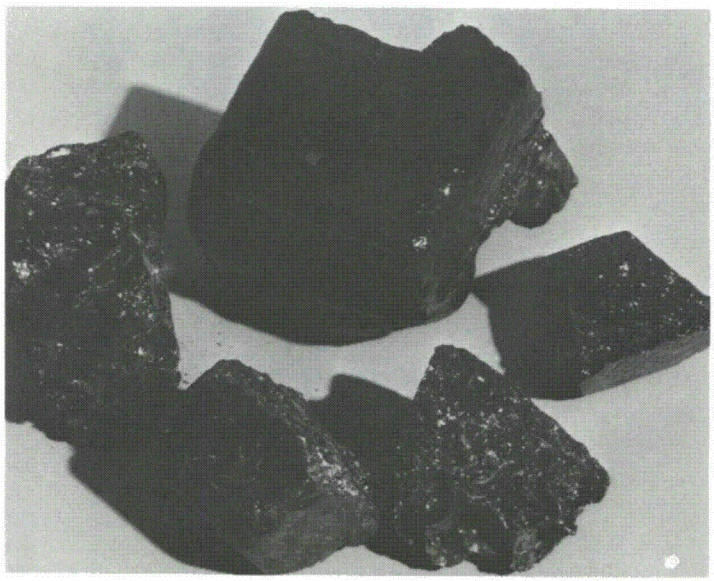
c. Run # 32B.
Additive: none.
1525°C.
60 min.
Water quench.





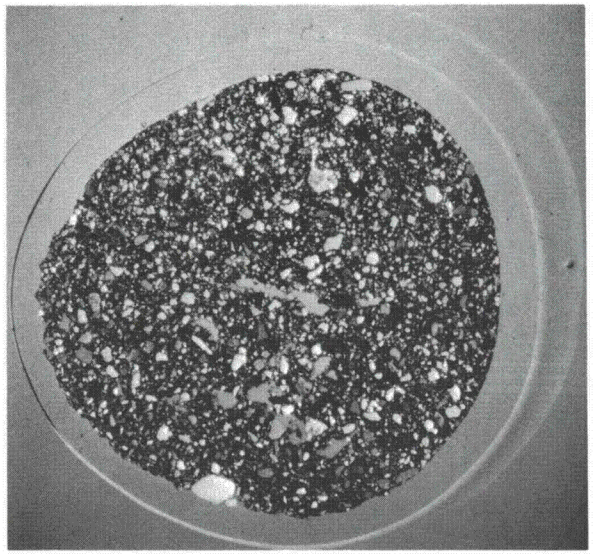


a. Run # 31.
Additive: 10% NaOH.
1100°C.
15 min.
Pan quench.

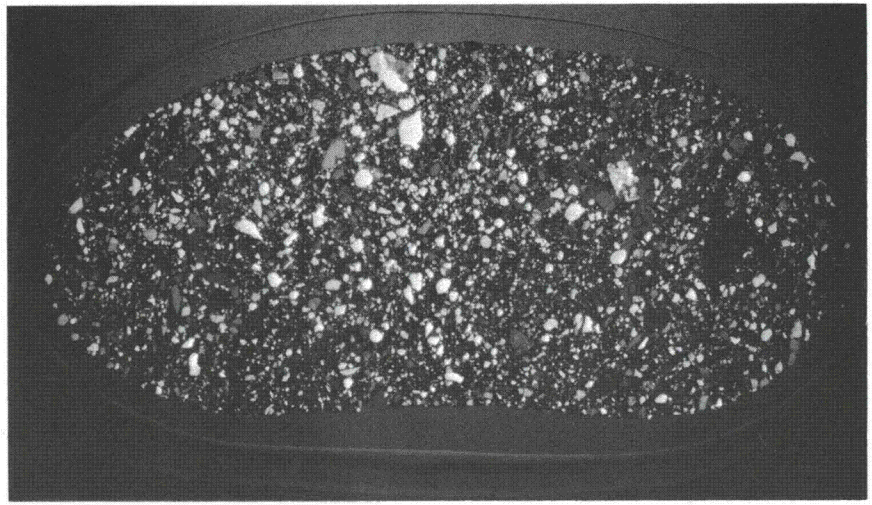


b. Run # 33.
Additive: borax.
1525°C.
30 min.
Ingot quench.

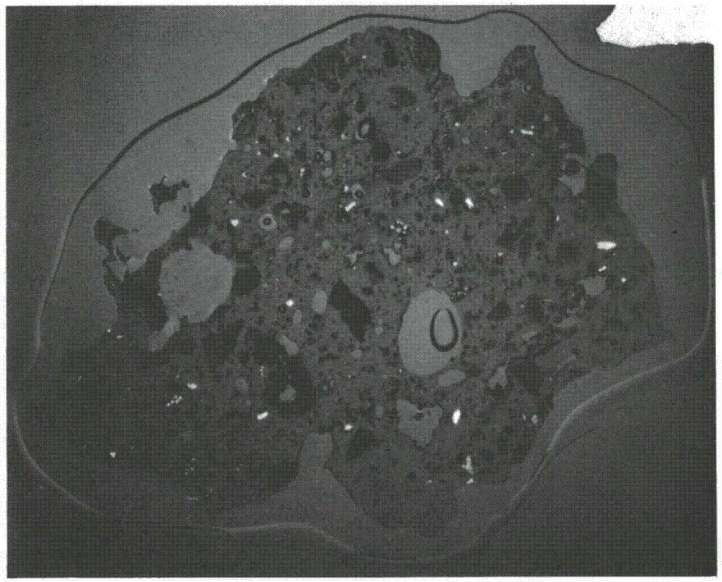
Fig. C-8. Vitrified Salt Lake City tailings (1100 and 1525°C)—NaOH and borax additives.



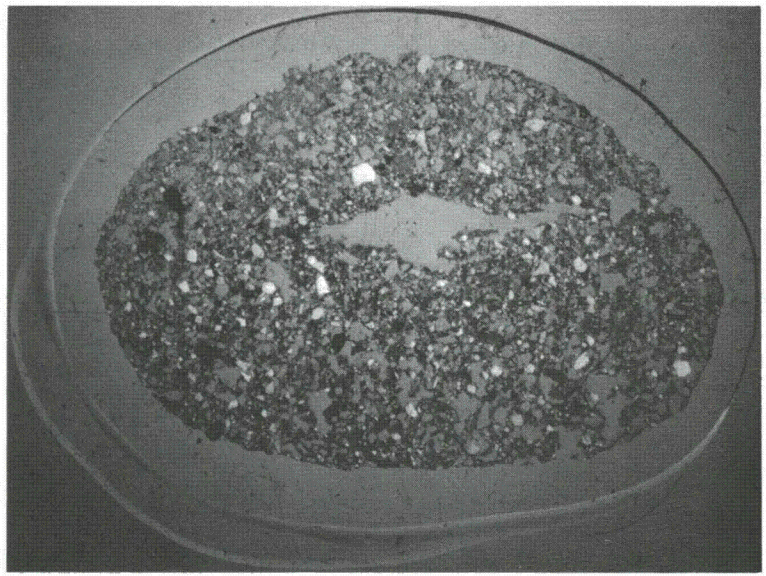
a. Run #3B (1000°C).



b. Run #9 (1050°C).

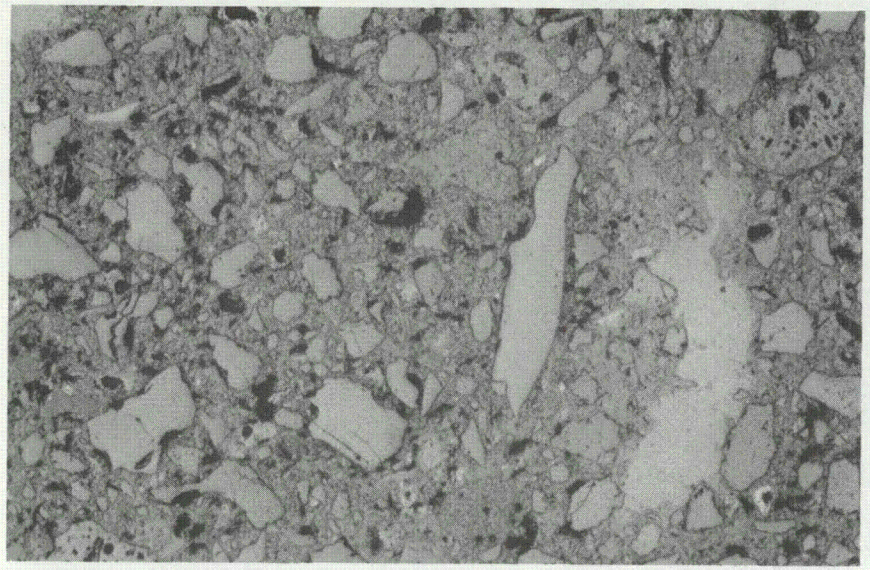


c. Run #2B (1400°C).

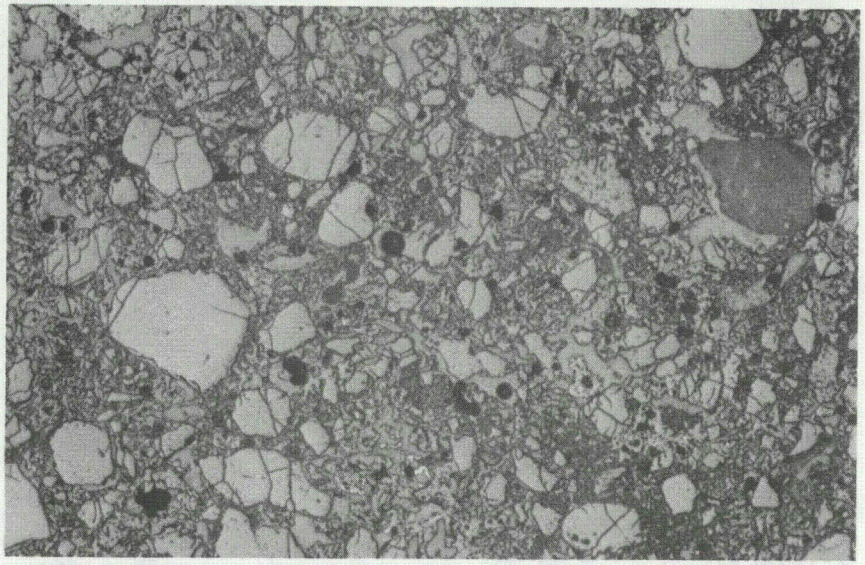


d. Run #14 (1100°C).

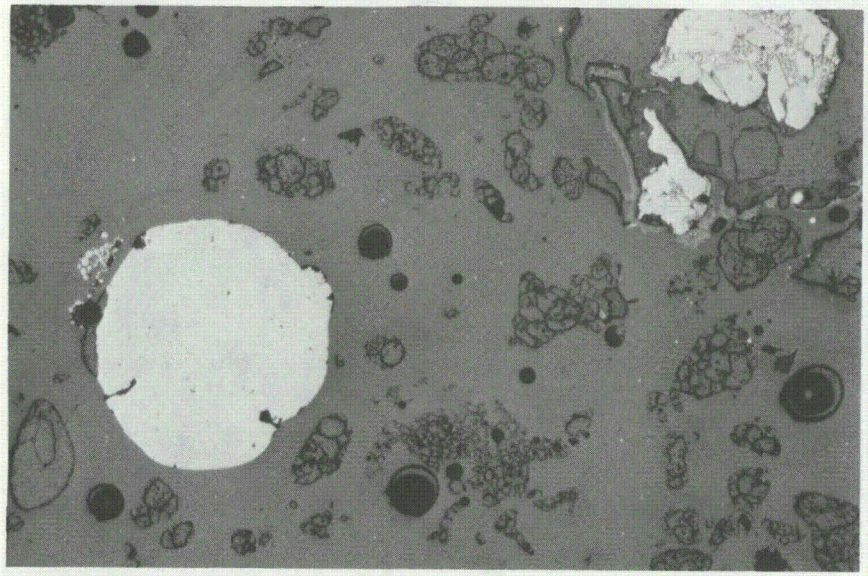
Fig. C-9. Photomicrographs (4.5X) of thin-sectioned, thermally stabilized tailings (AVG) agglomerates produced in the rotary furnace tests (1000 - 1400°C).



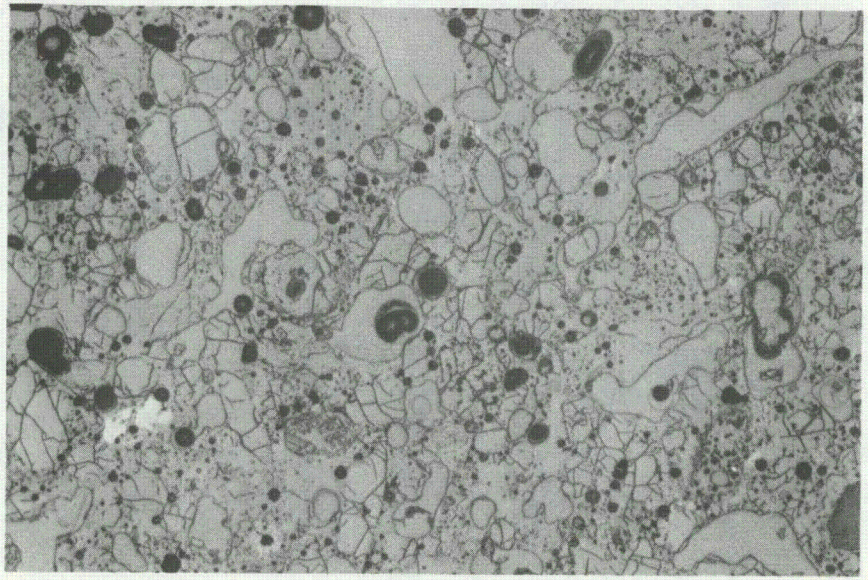
a. Run #3B (1000°C).



b. Run #9 (1050°C).

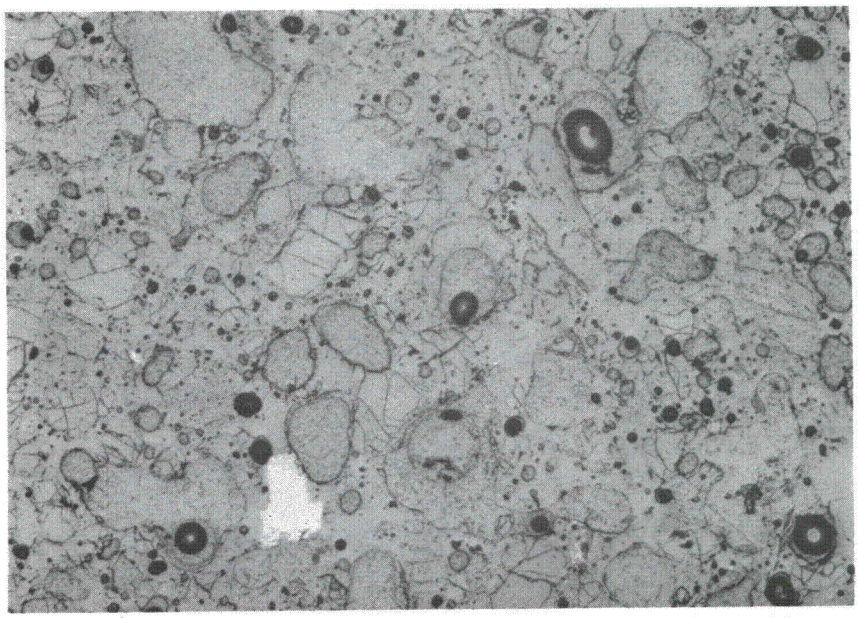


c. Run #2B (1400°C).

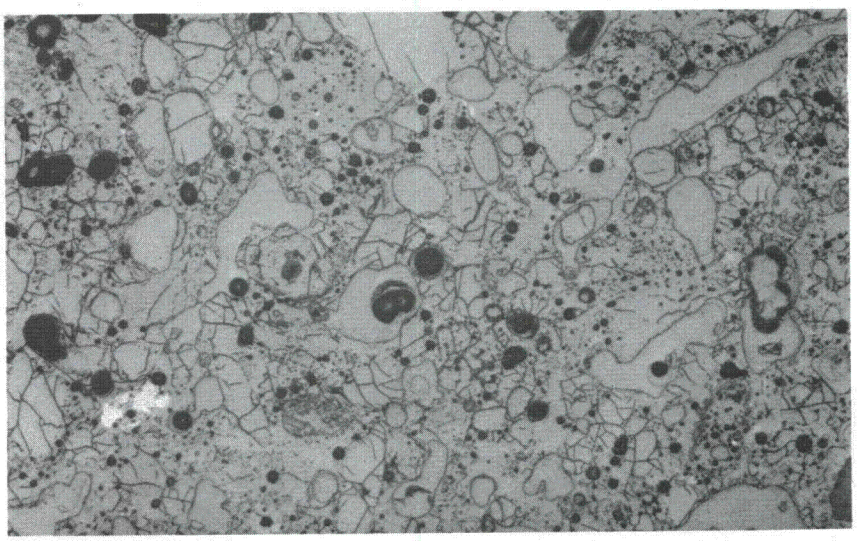


d. Run #14 (1100°C).

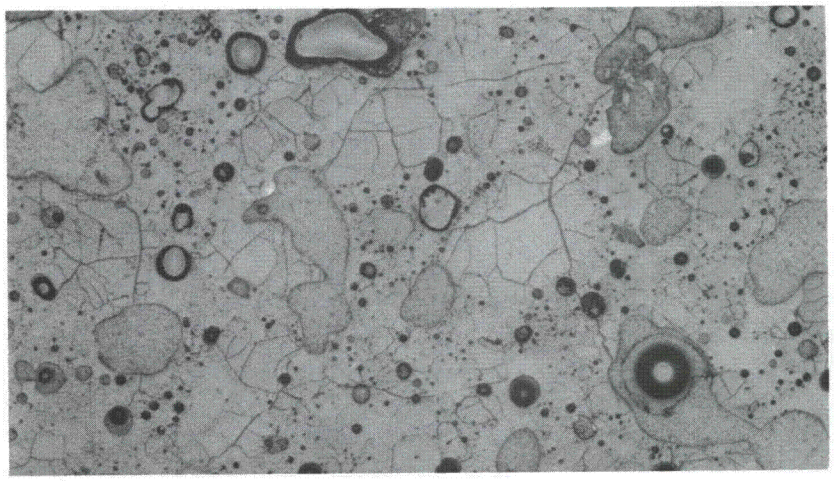
Fig. C-10. Photomicrographs (40X) of thin-sectioned, thermally stabilized tailings agglomerates shown in Fig. C-9.



a. Run #11, air cooled in ingot (slow).



b. Run #14, air cooled in pan (fast).



c. Run #13, water quenched (very fast).

Fig. C-11. Photomicrographs (40X) of thin-sectioned, thermally stabilized tailings agglomerates showing the effects of different quenches.

TABLE C-III

ENRICHMENT OF NONVOLATILE ELEMENTS AFTER THERMAL TREATMENT—A MEASURE OF WEIGHT LOSS

Test Run	Treatment Temperature (°C)	Concentration Ratio Output/Input Na	Al	V	Mn	U	Ca	Mean ± s
AVG								
#3E	1000	1.14	1.14	1.13	1.16	–	–	1.143 ± 0.013
#8	1050	1.13	1.14	1.15	1.18	–	–	1.150 ± 0.022
#12	1100	1.14	1.13	1.14	1.13	–	–	1.135 ± 0.006
#13	1100	1.11	1.13	1.11	1.22	–	–	1.143 ± 0.053
#14	1100	1.15	1.16	1.11	1.17	–	–	1.147 ± 0.026
#15	1075	1.13	1.16	1.13	1.14	–	–	1.140 ± 0.014
							Grand Mean	1.143
COAL								
#22	1000	1.21	1.19	1.21	1.15	1.17	1.20	1.188 ± 0.024
#23	1050	1.20	1.19	1.22	1.25	1.15	1.22	1.205 ± 0.034
#24	1075	1.24	1.23	1.25	1.21	1.17	1.21	1.218 ± 0.029
#27A	1100	1.26	1.23	1.27	1.25	1.24	1.23	1.247 ± 0.016
#27B	1100	1.25	1.24	1.23	1.23	1.17	1.20	1.220 ± 0.030
#27C	1100	1.23	1.20	1.22	1.31	1.21	1.18	1.225 ± 0.045
#28B	1100	1.24	1.23	1.24	1.31	1.21	1.22	1.242 ± 0.035
#28C	1100	1.23	1.20	1.23	1.22	1.21	1.21	1.217 ± 0.012
#29B	1100	1.24	1.21	1.25	1.27	1.26	1.19	1.237 ± 0.031
#29C	1100	1.23	1.21	1.23	1.18	1.21	1.21	1.212 ± 0.018
							Grand Mean	1.221

TABLE C-IV

LOSS OF VOLATILE CONSTITUENTS DURING THERMAL STABILIZATION

Input Material	Test Run	Treatment Temperature (°C)	Loss of Cl (%)	Loss of Cl (μg/g)	Loss of As (%)	Loss of As (μg/g)	Loss of Sb (%)	Loss of Sb (μg/g)	Loss of Se (%)	Loss of Se (μg/g)
AVG	#3E	1000	38	570	30	44	16	3	a	a
	#8	1050	49	730	53	79	21	4	a	a
	#12	1100	47	700	70	104	36	7	a	a
	#13	1100	49	740	70	104	26	5	a	a
	#14	1100	47	700	64	94	21	4	a	a
	#15	1075	41	620	26	39	5	1	a	a
COAL	#22	1000	39	550	34	45	39	7	35	4
	#23	1050	50	700	65	84	62	11	38	4
	#24	1075	56	780	66	85	55	9	47	5
	#27A	1100	59	825	74	96	62	11	-	-
	#27B	1100	58	815	67	87	60	10	46	5
	#27C	1100	57	805	67	87	62	11	48	5
	#28B	1100	66	930	79	102	66	11	59	6
	#28C	1100	62	875	81	106	69	12	55	6

[a]Analytical data erratic for AVG material, i.e., measurements on duplicate samples showed poor agreement.

TABLE C-V

EFFECT OF THERMAL STABILIZATION ON RADIONUCLIDE COMPOSITION

Test Run	Treatment Temperature (°C)	Treatment Time (min)	% Loss of ^{210}Pb	% Loss of ^{227}Ac[a]	% Loss of ^{227}Ac	% Loss of ^{234}Th[b]	% Loss of ^{230}Th	% Loss of ^{226}Ra[c]
AVG								
#8	1050	15	82	46	25	11	35	d
#14	1100	2.5	64	46	28	d	7	d
COAL								
#22	1000	15	84	33	29	d	d	2
#23	1050	15	89	37	29	6	2	2
#24	1075	15	91	33	29	2	d	4
#27B	1100	15	95	33	24	15	d	1

[a]As determined from ^{227}Th ($t_{1/2}$ = 18.2 d), time between treatment and counting ~90 days, i.e., 5 half-lives of ^{227}Th.
[b]Actually a measure of ^{238}U after a delay of ~4 half-lives.
[c]Measured directly from low-energy gamma.
[d]Sample enriched in radionuclide.

TABLE C-VI

EMANATING ^{226}Ra OF UNTREATED AND THERMALLY STABILIZED TAILINGS

Input Material	Sample ID	Temperature (°C)	Heatup Time (min)	Treatment Time (min)	Quench	Emanating ^{226}Ra ±95% CI	Emanation Reduction Factor
AVG	Untreated	–	–	–	–	102 ± 15	–
COAL	Untreated	–	–	–	–	110 ± 25	–
MIX	Untreated	–	–	–	–	84 ± 15	–
AVG	#3E	1000	20	35	Air	2.87 ± 0.60	36
	#8	1050	3	15	Air	1.18 ± 0.52	87
	#12	1100	3.5	2.5	Air	0.35 ± 0.06	290
	#13	1100	3	2.5	Water	0.49 ± 0.08	210
	#14	1100	4	2.5	Air	0.42 ± 0.08	240
	#15	1075	3	5	Air	0.47 ± 0.35	220
COAL	#22	1000	5	15	Air	0.51 ± 0.17	210
10% Coal	#23	1050	5	15	Air	0.33 ± 0.18	330
90% Tailings	#24	1075	4.5	15	Air	0.13 ± 0.06	840
	#27A	1100	5	15	Air	0.21 ± 0.08	520
	#27B	1100	5	15	Air	0.20 ± 0.02	550
	#27C	1100	5	15	Water	0.05 ± 0.06	210
	#28B	1100	5	30	Air	0.34 ± 0.14	320
	#28C	1100	5	30	Water	0.48 ± 0.13	230
	#29B	1100	7	60	Air	0.11 (n=1)	1000
	#29C	1100	7	60	Water	0.56 (n=1)	200
MIX	#19	1050	5	5	Air	0.79 ± 0.16	110
	#20	1100	5	16	Air	0.78 ± 0.28	110
Residual	#32A	1525	–	60	Air	0.05 (n=1)	2000
	#32B	1525	–	60	Water	0.03 (n=1)	3300

TABLE C-VII

PRE- AND POSTLEACH EMANATING ^{226}Ra FOR UNTREATED AND THERMALLY STABILIZED TAILINGS

Input Material	Sample ID	Preleach Emanating $^{226}Ra \pm 95\%$ Conf Interval (pCi/g)	Postleach Emanating $^{226}Ra \pm 95\%$ Conf Interval (pCi/g)	Postleach Emanating ^{226}Ra / Preleach Eamanting ^{226}Ra
AVG	Untreated	102 ± 15	150 ± 11	1.47[a]
COAL	Untreated	110 ± 25	126 ± 4	1.15
MIX	Untreated	84 ± 15	136 ± 5	1.62[a]
AVG	#13	0.49 ± 0.08	0.54 ± 0.02	1.10
	#14	0.42 ± 0.08	0.51 ± 0.04	1.21[a]
	#15	0.47 ± 0.35	0.60 ± 0.09	1.27
COAL	#27B	0.20 ± 0.02	0.90 ± 0.12	4.50[a]
	#27C	0.53 ± 0.06	0.95 ± 0.11	1.79[a]
MIX	#19	0.79 ± 0.16	2.24 ± 0.71	2.84[a]
	#20	0.78 ± 0.28	1.24 ± 0.35	1.59[a]

[a]Preleach and postleach means are significantly different ($P<0.05$) as determined by t-test of equality of means for samples with unequal variances and sample sizes.

TABLE C-VIII

CHARACTERIZATION OF LEACHATES OF UNTREATED AND THERMALLY STABILIZED TAILINGS

Input Material	Test Run Number	Leach Number	Cumulative Leachate Volume (m ℓ)	pH	Conductivity (μmhos/cm)	Eh (mV)	Conc (mg/ℓ) SO_4^{-2}	Ca	Na	Mg	Cl^-	K	Si	F^-	Mn
AVG	Untreated	1	88	7.05	2530	475	1560	510	66	57	43	29	17	4.1	2.7
		4	368	7.50	1870	436	1160	410	20	31	7.3	14	12	3.1	1.3
		8	704	7.25	2200	368	–	–	–	–	–	–	–	–	–
	#13	1	140	9.30	150	403	37	18	<10	0.66	7.6	3.5	8.5	<0.5	<0.03
	(1100°)[a]	4	558	9.30	46	384	1.2	6.8	<10	0.19	<1	<2	3.9	<0.5	<0.03
	(Water)	8	1085	9.25	50	385	–	5.5	<10	0.17	–	<2	2.8	–	<0.03
	#14	1	138	9.65	239	398	76	17	13	0.46	6.7	5.1	6.8	<0.5	<0.03
	(1100°)	4	537	8.70	44	420	3.1	6.1	<10	0.19	<1	<2	3.4	<0.5	<0.03
	(Air)	8	1052	8.55	41	416	–	4.8	<10	0.19	–	<2	2.7	–	<0.03
	#15	1	140	10.75	570	345	95	61	<10	0.25	3	3.5	9.7	<0.5	<0.03
	(1075°)	4	562	9.65	138	269	14.5	15	<10	0.22	<1	<2	6.5	<0.5	<0.03
	(Air)	8	1096	9.15	75	254	–	9.2	<10	0.28	–	<2	4.2	–	<0.03
COAL	Untreated	1	122	6.40	1940	435	950	370	47	46	37	20	13	3.9	1.2
		4	478	7.40	1550	325	790	330	15	21	2.8	11	12	2.9	0.8
		8	917	7.50	1400	356	–	–	–	–	–	–	–	–	–
	#27B	1	136	10.35	490	359	100	62	11	0.57	2	6.1	9.4	0.7	<0.03
	(1100°)	4	540	10.25	142	240	9.5	16	<10	0.22	<1	<2	5.3	<0.5	<0.03
	(Air)	8	1054	10.10	123	119	–	13	<10	0.21	–	<2	5.0	–	<0.03
	#27C	1	134	8.75	590	388	220	110	<10	3.1	8	6.8	4.5	<0.5	<0.03
	(1100°)	4	536	9.65	86	282	23	12	<10	0.30	<1	<2	3.8	<0.5	<0.03
	(Water)	8	1030	9.40	62	261	–	8.2	<10	0.29	<1	<2	3.4	<0.5	<0.03
MIX	Untreated	1	74	6.60	2680	472	1520	530	71	62	39	28	20	3.7	5.6
		4	317	6.75	2240	467	1470	500	24	36	8.7	13	14	3.1	2.2
		8	611	7.00	1840	467	–	–	–	–	–	–	–	–	–
	#19	1	132	11.10	1220	320	320	166	<10	0.15	2	4.6	6.6	1.0	<0.03
	(1050°)	4	539	10.10	560	381	120	76	<10	0.25	<1	<2	8.7	<0.5	<0.03
	(Air)	8	1043	9.90	260	374	–	31	<10	0.31	–	<2	10.1	–	<0.03
	#20	1	139	10.00	300	388	84	37	<10	0.59	<1	2.8	8.5	<0.5	<0.03
	(1100°)	4	556	9.45	100	385	41	13	<10	0.21	<1	<2	3.2	<0.5	<0.03
	(Air)	8	1082	9.00	72	322	–	10	<10	0.22	–	<2	2.5	–	<0.03

[a]Treatment temperature and quench type for each test run are presented in parentheses.

TABLE C-VIII (cont)

Input Material	Test Run Number	Leach Number	Cumulative Leachate Volume (mℓ)	pH	Conductivity (μmhos/cm)	Eh (mV)	Conc (mg/ℓ) Mo	U	Li	Al	P	Pb	V	As
AVG	Untreated	1	88	7.05	2530	475	3.1	1.3	1.4	1.05	0.79	0.75	0.42	0.35
		4	368	7.50	1870	436	2.2	3.7	1.0	0.80	0.81	0.51	0.32	0.38
		8	704	7.25	2200	368	1.8	1.8	–	–	0.91	–	–	0.37
	#13	1	140	9.30	150	403	0.47	<1	0.04	<0.05	0.26	<0.5	0.12	0.33
	(1100° Water)[a]	4	558	9.30	46	384	<0.2	<1	<0.03	0.16	<0.1	<0.5	<0.05	<0.2
		8	1085	9.25	50	385	<0.2	<1	<0.03	0.20	<0.1	<0.5	0.05	<0.2
	#14	1	138	9.65	239	398	0.80	<1	0.06	0.06	0.28	<0.5	0.84	0.29
	(1100° Air)	4	537	8.70	44	420	<0.2	<1	<0.03	0.15	<0.1	<0.5	0.09	<0.2
		8	1052	8.55	41	416	<0.2	<1	<0.03	0.09	<0.1	<0.5	0.05	<0.2
	#15	1	140	10.75	570	345	0.83	<1	0.13	0.63	<0.1	<0.5	1.2	<0.2
	(1075° Air)	4	562	9.65	138	269	<0.2	<1	0.03	0.19	<0.1	<0.5	0.15	0.42
		8	1096	9.15	75	254	<0.2	<1	<0.03	0.27	<0.1	<0.5	0.09	0.60
COAL	Untreated	1	122	6.40	1940	435	2.4	5.2	0.92	0.75	0.86	0.57	0.31	0.45
		4	478	7.40	1550	325	1.5	2.7	0.74	0.55	0.84	<0.5	0.27	0.44
		8	917	7.50	1400	356	0.89	<1	–	–	0.61	–	–	0.27
	#27B	1	136	10.35	490	359	0.73	<1	0.15	0.23	<0.1	<0.5	0.23	<0.2
	(1100° Air)	4	540	10.25	142	240	<0.2	<1	0.04	0.25	<0.1	<0.5	0.07	<0.2
		8	1054	10.10	123	119	<0.2	<1	<0.03	0.29	<0.1	<0.5	0.05	<0.2
	#27C	1	134	8.75	590	388	0.88	<1	0.19	0.10	0.14	<0.5	<0.05	<0.2
	(1100° Water)	4	536	9.65	86	282	<0.2	<1	<0.03	<0.05	<0.1	<0.5	0.09	<0.2
		8	1030	9.40	62	261	<0.2	<1	<0.03	0.13	<0.1	<0.5	0.06	<0.2
MIX	Untreated	1	74	6.60	2680	472	1.8	3.1	1.5	1.20	0.90	0.79	0.73	0.58
		4	317	6.75	2240	467	2.2	3.2	1.1	0.91	0.98	0.67	0.50	0.33
		8	611	7.00	1840	467	1.4	2.7	–	–	0.88	–	–	0.30
	#19	1	132	11.10	1220	320	2.5	<1	0.37	0.77	<0.1	<0.5	2.8	<0.2
	(1050° Air)	4	539	10.10	560	381	0.41	<1	0.14	0.39	<0.1	<0.5	0.54	<0.2
		8	1043	9.90	260	374	<0.2	<1	0.06	0.22	<0.1	<0.5	0.20	0.44
	#20	1	139	10.00	300	388	0.35	<1	0.08	0.07	0.14	<0.5	0.27	<0.2
	(1100° Air)	4	556	9.45	100	385	<0.2	<1	0.04	0.06	<0.1	<0.5	<0.05	<0.2
		8	1082	9.00	72	322	<0.2	<1	<0.03	0.07	<0.1	<0.5	<0.05	<0.2

TABLE C-VIII (cont)

Input Material	Test Run Number	Leach Number	Cumulative Leachate Volume (mℓ)	pH	Conductivity (μmhos/cm)	Eh (mV)	Conc (mg/ℓ) Ni	Zn	Fe	Co	Ba	B	^{226}Ra (pCi/ℓ)
AVG	Untreated	1	88	7.05	2530	475	0.29	0.34	0.22	0.13	0.14	0.08	127.3
		4	368	7.50	1870	436	0.13	0.11	0.14	<0.1	0.10	0.07	58.7
		8	704	7.25	2200	368	–	0.13	–	–	–	0.06	66.7
	#13	1	140	9.30	150	403	<0.1	<0.02	<0.1	<0.1	<0.02	0.08	8.1
	(1100°)[a]	4	558	9.30	46	384	<0.1	<0.02	<0.1	<0.1	<0.02	<0.02	8.5
	(Water)	8	1085	9.25	50	385	<0.1	<0.02	<0.1	<0.1	<0.02	<0.02	4.3
	#14	1	138	9.65	239	398	<0.1	<0.02	<0.1	<0.1	<0.02	1.1	7.5
	(1100°)	4	537	8.70	44	420	<0.1	<0.02	<0.1	<0.1	<0.02	0.04	8.3
	(Air)	8	1052	8.55	41	416	<0.1	<0.02	<0.1	<0.1	<0.02	<0.02	–
	#15	1	140	10.75	570	345	<0.1	<0.02	<0.1	<0.1	0.05	0.03	18.3
	(1075°)	4	562	9.65	138	269	<0.1	<0.02	<0.1	<0.1	0.03	<0.02	9.3
	(Air)	8	1096	9.15	75	254	<0.1	<0.02	<0.1	<0.1	0.06	<0.02	5.5
COAL	Untreated	1	122	6.40	1940	435	0.14	0.08	<0.1	<0.1	0.11	0.11	58.5
		4	478	7.40	1550	325	<0.1	0.10	<0.1	<0.1	0.10	0.09	68.9
		8	917	7.50	1400	356	–	0.08	–	–	–	0.03	18.7
	#27B	1	136	10.35	490	359	<0.1	<0.02	<0.1	<0.1	0.04	0.03	13.5
	(1100°)	4	540	10.25	142	240	<0.1	<0.02	<0.1	<0.1	<0.02	0.03	4.2
	(Air)	8	1054	10.10	123	119	<0.1	<0.02	<0.1	<0.1	<0.02	0.02	5.2
	#27C	1	134	8.75	590	388	<0.1	<0.02	<0.1	<0.1	0.05	0.06	24.3
	(1100°)	4	536	9.65	86	282	<0.1	<0.02	<0.1	<0.1	<0.02	<0.02	4.8
	(Water)	8	1030	9.40	62	261	<0.1	<0.02	<0.1	<0.1	<0.02	<0.02	2.5
MIX	Untreated	1	74	6.60	2680	472	0.82	1.10	0.19	0.37	0.13	0.20	80.2
		4	317	6.75	2240	467	0.32	0.37	0.12	0.12	0.12	0.08	95.3
		8	611	7.00	1840	467	–	0.12	–	–	–	0.05	35.7
	#19	1	132	11.10	1220	320	<0.1	<0.02	<0.1	<0.1	0.08	0.05	32.5
	(1050°)	4	539	10.10	560	381	<0.1	<0.02	<0.1	<0.1	0.07	0.02	27.7
	(Air)	8	1043	9.90	260	374	<0.1	<0.02	<0.1	<0.1	0.12	0.04	9.5
	#20	1	139	10.00	300	388	<0.1	0.05	<0.1	<0.1	0.04	0.07	14.9
	(1100°)	4	556	9.45	100	385	<0.1	<0.02	<0.1	<0.1	0.03	<0.02	10.3
	(Air)	8	1082	9.00	72	322	<0.1	<0.02	<0.1	<0.1	0.05	<0.02	4.6

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