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PILOT PLANT VITRIFICATION OF SIMULATED
ALPHA-CONTAINING ALKALINE WASTE

AUGUST 1971

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PILOT PLANT VITRIFICATION OF SIMULATED
ALPHA-CONTAINING ALKALINE WASTE

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August 1971

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PILOT PLANT VITRIFICATION OF SIMULATED ALPHA-CONTAINING ALKALINE WASTE

by J. D. Kaser

INTRODUCTION

This program was conducted to provide experimental process information on the vitrification of an alpha-contaminated waste sludge resulting from precipitating ferric hydroxide in certain Rocky Flats waste streams. Three pilot plant tests were performed on the semi-continuous melting of powdered sludge directly in waste containers.

SUMMARY AND CONCLUSIONS

The pilot plant tests demonstrated that the simulated sludge could be converted to an insoluble glass within 304L stainless steel storage containers. The molten waste did not corrode the containers significantly. During the melting process some dust, NO and water vapor are evolved. An off-gas condenser is probably not necessary, but a scrubber may be required to remove dust and NO. The melt is fluid and should be adaptable to intermittent discharge from a crucible into an unheated container.

PREPARATION OF SIMULATED SLUDGE

The typical composition of calcined sludge, as given to us by D. L. Ziegler in his letter of March 11, 1971, is shown in Table 1. For reasons of safety and economy beryllium and gallium were omitted from our simulated waste formulation.

A major ingredient in the waste sludge is Dicalite #4106 filter aid. The chemical composition of this material, as given in Table 2, was supplied to us by J. C. Horsley of the Dicalite Div. of Grefco, Inc.

TABLE 1. Typical Analysis of a Calcined Waste Sludge
(50:50 Mixture of 1st and 2nd Stage Sludge)

	<u>wt%</u>	<u>(wt% without BeO or Ga₂O₃)</u>
Al ₂ O ₃	6.21	6.37
BeO	0.40	----
BaO	0.01	0.01
CaO	18.84	19.33
Cr ₂ O ₃	0.08	0.08
CuO	0.27	0.28
Fe ₂ O ₃	5.53	5.67
K ₂ O	3.53	3.62
MgO	6.19	6.35
Na ₂ O	11.21	11.50
NiO	0.14	0.14
PbO	0.69	0.71
P ₂ O ₅	1.56	1.61
SiO ₂	43.13	44.25
TiO ₂	0.06	0.06
ZnO	0.02	0.02
Ga ₂ O ₃	2.13	----
	<hr/>	<hr/>
	100.00	100.00

TABLE 2. Composition of Dicalite Perlite Filter Aid
(Produced at Antonito, Colo.)

	<u>wt%</u>
SiO ₂	65.9
Al ₂ O ₃	15.5
K ₂ O	9.5
Na ₂ O	7.8
Fe ₂ O ₃	0.78
CaO	0.19
MnO ₂	0.16
TiO ₂	0.12
MgO	0.053
PbO	0.025
ZrO ₂	0.02
Ga ₂ O ₃	0.013
Cr ₂ O ₃	0.0035
B ₂ O ₃	0.001
CuO	0.001

The Dicalite was used as the sole source of silicon in the simulated sludge. However, due to the large amounts of other elements in the Dicalite it was not possible to exactly reproduce the composition in Table 1 without using some other source of silicon. Nevertheless, using only Dicalite filter aid to supply silicon, a simulated sludge recipe was devised with a composition reasonably approximating the typical sludge composition. The calculated sludge composition from this recipe is given in Table 3. This composition has more aluminum and potassium and less calcium and iron than the composition in Table 1.

In order to approximate the chemical environment in which the actual sludge was precipitated and dewatered, the following criteria were followed:

1. The waste solution before precipitation of the sludge should be a 7N acid solution containing about 10 wt% dissolved solids and 100 ppm Cl^- ; 5000 ppm F^- and 500 ppm SO_4^{2-} .
2. The sludge should be precipitated by adding 7N NaOH solution until pH 11 is reached.
3. The final separated sludge with filter aid should contain about 60 wt% water.

To meet these criteria the following procedure was used to produce a batch of simulated sludge with filter aid:

1. These chemicals were dissolved in 166 liters of 7N HNO_3 solution:

$\text{Ba}(\text{NO}_3)_2$	3.25 g
$\text{Ca}(\text{NO}_3)_2$	21 lb
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	68.04 g
$\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	175.8 g
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	9.7 lb
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	15 lb

TABLE 3. Calculated Composition of Simulated Calcined Waste Sludge
Used in This Study

	<u>wt%</u>
Al_2O_3	10.30
BaO	0.01
CaO	15.90
Cr_2O_3	0.07
CuO	0.23
Fe_2O_3	4.70
K_2O	6.33
MgO	5.15
Na_2O	11.40
NiO	0.11
PbO	0.57
P_2O_5	1.26
SiO_2	43.90
TiO_2	0.05
ZnO	0.02
	<hr/>
	100.00

NaF	374	g
Na ₂ SO ₄	10.5	g
Ni(NO ₃) ₂ ·6H ₂ O	93	g
Pb(NO ₃) ₂	179.2	g
TiCl ₄	23.8	g
Zn(NO ₃) ₂ ·6H ₂ O	12.5	g
H ₃ PO ₄ (75%)	485	g

2. While the solution was being agitated, 7N NaOH was added until the pH was between 10 and 12.
3. Then 30.5 lb of Dicalite #4106 Filter Aid was added. During the addition of NaOH solution, the solution temperature was allowed to rise to approximately 150 °F. A cleaner separation of sludge was obtained from a hot solution than from a cold solution. Twelve batches of simulated sludge were made using this recipe and procedure.

The sludge was separated from the solution with a 6-inch Bird continuous centrifuge. Two samples of the sludge had moisture contents of 60 and 70 wt%. Initially the centrifuge effluent contained a great deal of suspended solids. However, a clear effluent was obtained by rearranging the discharge bushings to obtain the maximum effluent pool depth, and by keeping the slurry at about 150 °F. The centrifuge speed was 7800 rpm and the average liquid throughput rate was 0.75 gpm.

After centrifugation the sludge was spread out on plastic sheets and sun dried until the moisture content was below 3 wt%. The dried sludge was then pulverized in a hammer mill. Simulated leach residues supplied by Rocky Flats were also pulverized in a hammer mill and then were mixed with the simulated sludge in the proportion of 11 lb of simulated leach residues to 89 lb of dried simulated sludge. Blending was performed in a small concrete mixer. The simulated leach residues contained the following material:

	<u>lbs</u>
Leached incinerator ash	9.2
Leached insulation	19.8
Glass	15
Slag (CaF_2)	4.5

PROCESS DESCRIPTION

Dried and powdered sludge was mixed with borax, ground glass, insulation, incinerator ash and slag (CaF_2) and metered into the waste container by a vibrating trough solids feeder. The powdered solid fell from the vibrating trough into an open funnel and then through a two-inch diameter pipe into the dust deentrainment chamber and finally into the waste container where the powder melted. The gas, evolved during the melting process, along with air drawn in through the solids addition line, passed through a condenser and a packed tower caustic scrubber where the oxides of nitrogen were absorbed.

At the end of each run the electrical resistance furnace was turned off and the molten waste cooled to form a coherent glassy solid.

MELTING POINT DETERMINATION

Various mixtures of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and simulated dried sludge plus leach residues were placed in alumina crucibles. A thermocouple was immersed in each powder mixture. The mixtures were heated in a high temperature oven and the temperature rise of the samples with time was recorded on a potentiometric multipoint temperature recorder.

In the first series of measurements the sludge mixtures contained 20, 30 and 40 wt% borax. The mixtures were heated to 900 °C and all the mixtures melted. There was no sharp melting point as evidenced by the lack of any inflections on the temperature-time curves.

A second series of melting tests was attempted using sludge

mixtures containing 0, 5, 10 and 15 wt% borax. In these tests the furnace temperature did not exceed 800 °C, because a heating element failed and none of the mixtures melted completely. The series was repeated in another furnace where the temperature reached 1050 °C and all the mixtures melted completely. The information obtained from these melting tests can be summarized as follows:

<u>Wt% Borax</u>	<u>Melting Point</u>
0-15	Between 800 and 1050 °C
20-40	Less than 900 °C

PILOT PLANT EQUIPMENT

The solids feeder consisted of a 60° hopper mounted on an electrically vibrated trough 2 inches wide and 16 inches long. The solids feed rate could be controlled three ways: (1) by varying the clearance between the hopper bottom and the trough, (2) by varying the amplitude or intensity of the vibrations and (3) by changing the slope of the trough. In the pilot plant tests the trough was kept level and the clearance between the hopper bottom and the trough was kept at about one inch. When the clearance was less, lumps of leached insulation accumulated at the bottom of the hopper and slowed the solids discharge rate. The feed rate was primarily controlled by adjusting the current to the vibrator motor with a rheostat.

The pipe conveying the powder into the waste container was 2 inches ID and 3 feet long; it sloped about 45°. A small vibrator was attached to the pipe to prevent powder accumulation.

The deentrainment chamber was an inverted truncated cone of stainless steel 30 inches high, with a top diameter of 20 inches and a bottom diameter of 8 inches. There were two quartz windows in the top of the chamber so that the melting process could be viewed.

The waste containers or pots were 60 inches high and made from sections of 8-inch schedule 40 304L stainless steel pipe with 3/8-inch

304L stainless steel plate welded to the pipe to form a bottom. An internal axial thermowell was made of 1-inch schedule 80 304L stainless steel pipe. These containers were used because they were available as surplus equipment from another program. It is likely that a cheaper alloy could be found that would be suitable for containing melting sludge.

The pot furnace was a single zone nichrome element electrical resistance furnace designed for a maximum power input of 75KW. Overall length of the furnace was 55 inches with a heated length of 43 inches. Internal diameter of the furnace was 19 inches. It was insulated with 8 inches of firebrick.

The off-gas condenser was stainless steel with a stainless steel tube bundle providing about 10 ft² of heat transfer area. Cooling water exit temperature was approximately 80 °F and the off-gas exit temperature was about 90 °F.

The caustic scrubber consisted of a 6-inch diameter column packed with 6 feet of 1-inch Raschig rings. Fifteen gallons of 6M NaOH solution were used to absorb oxides of nitrogen from the off-gas.

PROCEDURE FOR THE PILOT PLANT TESTS

After the off-gas suction system was turned on and the furnace reached the desired operating temperature, powdered sludge and flux mixture was loaded into the solid feeder hopper and the feeder was turned on as well as the vibrators for preventing powder hang-up and plugging.

Since the powder inlet was always open, the system was kept under a slight vacuum to prevent large amounts of fumes (oxides of nitrogen) escaping through the powder inlet into the room.

The melting capacity or maximum feed rate was determined by observing the surface of the melt. When the feed rate was too high the surface became dark because it became covered by cool powder.

accumulating faster than it could be melted. When this happened the feed rate was reduced until an incandescent surface again could be observed. Thus the operating feed rate was somewhat less than the maximum feed rate. The feed rate was adjusted several times during each run so that it was always close to the maximum rate. The average feed rate during a run was determined from the total feed consumption and the total operating time of the feeder.

Three or four times during each run the off-gas was sampled. A known amount of off-gas was drawn through an 0.8 micrometer filter and then through a self-flushing gas sample bottle. The flow rate of off-gas through the sampler was measured with a small rotometer. Solids collected on the filter were weighed and the composition of the off-gas samples was determined by mass spectrometry.

At the end of the first and third run the furnace was shut off when the solid feeder was turned off. At the end of the second run the furnace was left on so that the container was kept at the operating temperature for a total of 72 hours to magnify any possible corrosion.

When the furnace was cooled, the container was removed and cut open for inspection of the container and product.

PILOT PLANT TEST RESULTS

Table 4 summarizes the results of the three pilot plant tests. They showed that a large volume reduction could be obtained. A dense glassy product was obtained which did not corrode the container appreciably and which had a very low solubility in water. The melting capacity appears to be limited by the rate of heat transfer from the hot container walls to the powder. We could not discern whether the powder floated on top of liquid during melting or whether it sank into the molten sludge. Very little condensible vapor (water) was given off in the process. Due to the decomposition of the sodium nitrate in the sludge, considerable amounts of nitrogen oxides were evolved as

TABLE 4. Summary of Pilot Plant Test Data

	Run 1	Run 2	Run 3
Percent Borax	20	20	0
Feed Consumed, lb	20	82	64.7
Operating Time, hr	5.5	15.6	14.6
Avg Feed Rate, lb/hr	3.6	5.3	4.5
Feed Density (lb/ft ³)	49.8	49.8	47.4
Product, lb	13	53	40
Product Density (lb/ft ³)	158	163	170
Product Vol., ft ³	0.085	0.325	0.236
Volume Reduction Factor, Vol. Feed/ Vol. Product	4.8	5.1	5.8
Nitrogen Absorbed by Caustic Scrubber, lb	Not Measured	Not Measured	0.76
Operating Temp., °F	1740	1920	1920
Time at Operating Temperature	5.5	32	28
Leachability, mg/cm ² -day	0.0029	0.0029	0.0001
Corrosion, mils	<10	<10	<10
Dust Content of Off- Gas, lb/ft ³	Not Measured	0.0002	0.0002

evidenced by the uptake of nitrogen by the caustic scrub solution.

Because some of the powder accumulated on the inside surfaces of the equipment where it was periodically dislodged by the vibrators, the delivery of powder to the melt surface was erratic and, consequently, the NO content of the off-gas fluctuated over a wide range. For this reason no meaningful quantitative information could be derived from the analyses of the off-gas samples. However, the mass spectrographic analyses did reveal that NO was the only oxide of nitrogen present in the off-gas. The amount of NO in the off-gas samples varied from 0.04 to 6.27 mole %. The balance of the off-gas was air.

The high-silicate melts appeared to flow readily at the operating temperatures (1740-1920 °F), so that these melts should be easy to discharge from a crucible or separate melter into a cold storage container.

For the leachability measurements, 3/4 inch polished cubes were prepared from the vitrified product of the pilot plant tests. The samples were immersed in triple distilled water which was slowly recirculated at room temperature. The weight loss rate was measured by weighing the dried samples after known time intervals. The samples were dried at 110 °C until a constant weight was attained.

RECOMMENDATIONS

There are two potential improvements in the process which we feel warrant further attention:

1. Use of a continuous centrifuge rather than a filter could eliminate the need for copious amounts of filter aid, and result in a substantial reduction in waste volume. A modest pilot plant testing program should determine the feasibility of this approach.
2. Recovery of gallium from the sludge may be of substantial economic benefit. According to the sludge analysis given

in Table 1, each ton of calcined sludge contains about 14Kg of gallium worth approximately \$14,000. If the gallium can be leached from the sludge by strong caustic solution as the gallate ion, there are well developed processes for extracting gallium from the caustic solution.*

* Kirk-Othmer Encyclopedia of Chemical Technology, second edition, Volume 10, pp. 311-328. Interscience Publishers, New York, 1963.

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