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RECOVERY OF CARBON VALUES FROM HORIZONTAL ZINC RETORT RESIDUES

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ABSTRACT

Old horizontal and vertical retort Zn smelter sites are being examined by Federal and State environmental agencies because the residues and other wastes contain Pb and Cd. Residues at some of the sites have been declared hazardous wastes. Conservative estimates place the amount of these wastes at 36 Mmt. There are a number of sites with up to 0.4 Mmt of wastes in Kansas, Illinois, and West Virginia and one in Pennsylvania with 27 Mmt of wastes. In addition to their C content (20-30%), the residues represent a possible resource for Ge, Ga, In, Ag, Mn, Pb, and Zn. Samples obtained from several sites near Gas, Kansas are being used in research attempting to recover the unburned C and the metal values as separate products, leaving a nonhazardous residue that could be disposed of safely and economically. The residue was ground to liberate the C. Initial efforts to recover the C used oil agglomeration. This method recovered 67-78% of the C at grades of 66-79% but required large quantities of oil; the absence of agglomeration made separation difficult. Froth flotation has recovered 64-85% of the C in concentrates grading 54-84%.

INTRODUCTION

The U.S. Bureau of Mines has been conducting research on the residues from horizontal retort zinc smelters as part of its effort to reduce the environmental and economic impact of wastes contaminated with heavy metals. If the estimated 36 Mmt of horizontal and vertical retort residues were classified as hazardous wastes, the disposal costs could exceed $8 billion. If the wastes could be rendered nonhazardous, disposal costs could be reduced to about $400 million. Treatment of these wastes to recover the C and metal values would reduce the volume of material requiring disposal and may recover usable byproducts to help offset the treatment cost.

A typical horizontal retort furnace, as shown in cross section in Figure 1 (1), contained hundreds of cylindrical fireclay retorts, heated with coal or gas. The retorts were charged with calcined or sintered Zn concentrates plus an excess of coal or coke to reduce the ZnO and to maintain a reducing atmosphere so the Zn vapors could be collected in the attached condenser as liquid Zn (2-6).

About 93 smelters were operated in 13 states in the late 1800s to the mid 1900s (5-10). The last primary horizontal retort plant closed in 1976, and the last primary vertical retort plant closed in 1981. All of these sites represent some degree of environmental or health hazard, depending on the quantity of residues remaining, the extent to which they are exposed, and their composition. Many of the old smelters may also have contaminated the soil in the surrounding area if Zn and Cd fumes leaked from their condensers. Produce and other crops grown in soils with elevated Cd levels can pose a significant health hazard (11).

Of the 39 old smelter sites in Kansas and Missouri that were reported in various references (5-10), one has been capped, one is part of a regional Superfund site, 11 have been completely built over, 12 have exposed and scattered wastes of unknown depth and quantity, 7 have open piles containing large quantities of wastes, and the remaining 7 will require additional record searches or fieldwork to locate. Another 54 smelters were located in Colorado, Texas, Oklahoma, Arkansas, Illinois, Indiana, Tennessee, Pennsylvania, Virginia, West Virginia, and New Jersey.

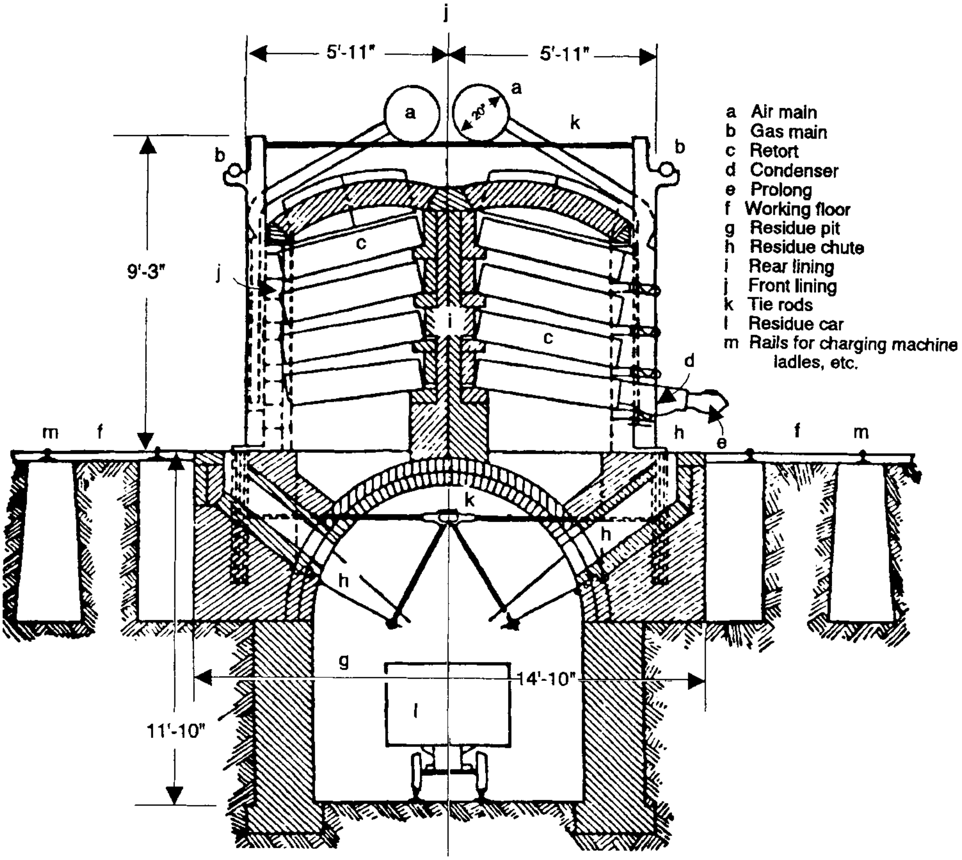

FIGURE 1. Typical horizontal retort furnace

SAMPLE CHARACTERIZATION

Small samples of residue from two of the smelter sites south of Gas, Kansas were used in the preliminary characterization and treatability studies. Three fractions of each sample were needed for chemical analysis. Carbon was determined with a carbon-sulfur analyzer. Digestion with HNO_3 and H_2O_2 was used to dissolve As, Cd, Cu, Ag and other metals. Peroxide fusion was required for complete extraction of Fe, Pb, Zn, and the other refractory elements. The resulting solutions were analyzed by atomic absorption or inductively coupled plasma spectrometry. Analyses of the two original residue samples are given in Table 1.

Qualitative emission spectrographic analysis of the residue samples indicated that Fe was the only preponderant (>10%) element, with Pb, Si, and Zn present as minor (0.1-10%) elements and Al, B, Ba, Ca, Cr, Cu, Mg, Mn, Ni, V, and Zr as trace (<0.1%) elements. X-ray diffraction analysis of the retort residues found SiO_2 (quartz), Fe_3O_4 (magnetite), $3Al_2O_3 \cdot 2SiO_2$ (mullite), $ZnFe_2O_4$ (franklinite), and $ZnAl_2O_4$ (gahnite) were present.

Some of the horizontal retort Zn smelters used magnetic separation to upgrade and recover the metal values from their retort residues. Portions of the initial residue samples were split out, pulverized to 100% minus 30 mesh particle size and wet-screened at 400 mesh. The 30X400 mesh material was dried and then processed with a hand magnet (magnetic fraction M1) and a dry magnetic separator at three different current settings (fractions M2-M4). The remainder was the nonmagnetic fraction (NM). The high C content of the magnetic fractions indicated a high degree of locking between the C and the magnetic phases, as shown in Table 2. Another portion of residue from one of the sites was pulverized to 100% minus 100 mesh and then processed the same way. As can be seen from Table 2, this did not eliminate the locking problem.

Polished sections of size fractions and magnetic fractions of the residue were examined visually with a polarizing microscope. Examination of the 200X400 mesh size fraction showed that most of the particles were locked, rimmed, or complex-multiple-phase mixtures. Selected particles and representative areas of the size and magnetic fractions were photographed before the mounts were submitted for scanning electron microscopy (SEM) studies. Both energy dispersive and wavelength dispersive X-ray analysis were used in the SEM. Zinc appeared to be present in these samples as Zn metal, Zn-Cu alloy, oxide, mixed oxide with Mn or Mn plus Fe, aluminate, silicate, mixed aluminosilicate with Fe, and a sulfide or

TABLE 1. ANALYSIS OF INITIAL RESIDUE SAMPLES

Element	Sample		Element	Sample	
	D5	D7A		D5	D7A
Si (%) . .	17.5	15.2	Pb (%) . .	1.44	1.90
C (%) . .	13.8	17.6	Mn (%) . .	0.60	0.59
Fe (%) . .	10.8	17.0	S (%) . .	0.46	0.46
Al (%) . .	7.0	3.3	As (ppm) .	254	684
Zn (%) . .	5.1	4.3	Cd (ppm) .	168	140

TABLE 2. CARBON GRADE IN MAGNETIC FRACTIONS (%)

Fraction	Sample		
	D5	D7A	D7A
	30X400 Mesh		100X400 Mesh
M1 . . .	5.6	6.7	7.7
M2 . . .	23.8	28.1	25.4
M3 . . .	22.2	31.4	37.2
M4 . . .	8.3	45.1	38.5
NM . . .	17.6	37.6	45.8

sulfate. Iron was observed as oxide, silicate, mixed silicate with Ti and Zn, alloy or oxide with Mn, and a mixed sulfide or sulfate with Zn. Lead was present as metal, alloyed with As, silicate, oxide, mixed oxide with Mn, and a mixed sulfide or sulfate with Fe. A number of small Ag particles were found, both free and as inclusions in larger particles. The Ag was found in an alloy with Pb and Cu, a silicate, and a sulfide or sulfate with Fe. A few phases high in Cd, Ba, or Zr were located. Several areas that were high in La and Ce were detected. The C particles frequently had partial or complete Fe rims. Many of the C particles also appeared to be partially reacted since they contained Pb, S, and other elements and the rims or the whole particle appeared to contain no more C than the epoxy in which they were mounted.

In October 1991, auger drill samples of retort residue were collected at two of the smelter sites south of Gas, Kansas. Samples of high-Fe residue (found as large cemented masses), retort, condenser, and slag were also obtained. Substantial quantities of clean common brick, firebrick, and miscellaneous refractories were also found at the sites but not sampled. The retort residue samples were dried and screened, and the oversize crushed to minus 6.4 mm. The moisture content of the samples ranged from 5.0-29.7%. Head samples were split from each residue sample and small portions were split out, pulverized, and submitted for analysis.

Analysis of the individual retort residue samples showed that they contained 9.8-37.3 C, 6.6-22.5 Fe, 1.2-10.7 Zn, 0.7-3.6 Pb, 0.08-1.2 Mn, and 0.04-0.44% Cu, and 87-2,000 ppm As, 20-340 ppm Cd, and 22-236 ppm Ag. Composite samples from the two smelter sites were prepared by blending the individual samples. Analyses of the two composite samples are given in Tables 3 and 4.

The composite samples were also subjected to the Toxicity Characteristic Leaching Procedure (TCLP, EPA method 1311). Both samples failed for both Pb and Cd, as shown in Table 5.

Representative portions of the composite samples were wet-screened at 400 mesh. The plus 400 mesh fractions were dried and screened. Samples of the screen fractions were analyzed. Both composites exhibited the same general distribution of elements among the size fractions. Carbon and, to a lesser extent, Zn, tended to concentrate in the plus 30 mesh fractions while Ag, As, Cd, Cu, Fe, Pb, and Mn tended to accumulate in the minus 30 mesh fractions.

Samples of used refractories, slags, and high-Fe residue from the smelter sites near Gas, Kansas were also analyzed and subjected to the TCLP. Three samples of retort, one sample of retort with a heavy layer of attached slag, three different samples of slag, and a sample of slaggy residue all passed the TCLP. A sample of condenser failed the test for both Pb and Cd. A fourth sample of slag failed because of Cd. A sample of a well-used, more porous

TABLE 3. ANALYSIS OF COMPOSITE SAMPLES (%)

Element	Sample		Element	Sample	
	D6C	D7C		D6C	D7C
C . . .	23.0	19.6	Si . .	1.22	1.38
Fe . .	16.8	12.5	Ca . .	0.75	1.17
Zn . .	4.4	5.2	S . . .	0.66	0.45
Al . .	3.14	4.75	Mg . .	0.32	0.40
Pb . .	2.21	1.77	Mn . .	0.26	0.46

TABLE 4. ANALYSIS OF COMPOSITE SAMPLES (ppm)

Element	Sample		Element	Sample	
	D6C	D7C		D6C	D7C
Cu	2,628	1,006	Cr	116	48
In	354	294	Ce	106	103
As	233	859	Zr	85	125
V	180	162	Ga	66	65
Ge	176	174	Ni	60	63
Ag	150	70	Sb	0.6	0.5
Cd	80	159			

TABLE 5. ANALYSIS OF TCLP EXTRACTS FROM COMPOSITES (ppm)

Element (EPA Limit)	Sample		Element (EPA Limit)	Sample	
	D6C	D7C		D6C	D7C
Pb (5) . . .	52.5	41.5	Se (1) . . .	0.12	0.20
Cd (1) . . .	1.26	3.32	Ag (5) . . .	0.011	0.008
Ba (100) . .	0.32	1.14	Hg (0.2) . .	<0.2	<0.2
Cr (5) . . .	0.64	0.69	As (5) . . .	<0.06	<0.06

retort from an adjacent site and a sample of high-Fe residue failed for Pb. The high-Fe residue was expected to be similar to the other residue samples in failing the TCLP. However, it was hoped that the condenser and retort fragments would pass the test so they could be disposed of after separation from the residue by screening.

Five of the eight samples that passed the TCLP have Pb contents above 500 ppm, which may prohibit surface disposal on the sites. In the past, large quantities of these smelter wastes were used for road fill. Materials that fail the TCLP are classified as hazardous waste. Those that pass the TCLP but exceed the 500- to 1,000-ppm Pb content limit originally proposed by the Centers for Disease Control, and adopted by the U.S. Environmental Protection Agency, may not be used in areas where people would come in contact with them (12).

OIL AGGLOMERATION

Oil agglomeration has been used to recover coal fines. The coal slurry is intensely mixed with an oil that attaches to the coal particles and causes them to agglomerate. The agglomerated coal is then allowed to float to the surface for recovery, leaving the dispersed ash particles behind (13).

Initial Tests

Preliminary oil agglomeration tests on pure C indicated that kerosene, olive oil, rapeseed oil, and castor oil would all be suitable. Castor oil was selected for additional testing because it was the only candidate that could be removed with alcohol. This simplified the preparation of samples for chemical analysis.

The initial oil agglomeration tests were run with 20-g portions of 100% minus 60 mesh sample D7A and 180 mL of water in a beaker with an overhead stirrer. The C recovery, using castor oil at room temperature, was <2%. Neither adjusting the slurry pH nor using kerosene instead of castor oil improved the recovery. Switching to a 100X400 mesh fraction of the same sample improved the recovery somewhat. The C product from these tests was not agglomerated; upon standing it rose to the surface as a slurry that stuck to glass, stainless steel, polyethylene, and fluoropolymers. Adding the oil in small doses did not promote agglomeration.

The results of an oil agglomeration test on minus 100 mesh coke breeze indicated that oil additions of up to 25% by weight of the C in the sample might be necessary for good recovery. A variety of samples, size fractions, preparation methods, and reagents were tested in an effort to improve the C recovery. These tests recovered <1% of the C.

Bench-Scale Tests

Although the initial agglomeration tests were not successful, bench-scale oil agglomeration tests were conducted to determine the effect of improved agitation. These tests were run with castor oil and representative portions of the composite residue sample D7C. The residue sample (150 or 300 g) was ground with water in a small stainless steel rod mill and the resulting slurry was transferred to a modified flotation cell which provided high-shear agitation. In each test oil was added to the slurry and mixed for 4 min. The slurry was then allowed to settle while the C and oil rose to the surface. The C and oil concentrate was skimmed off. This process was repeated until the oil and C layer was too thin to recover. At this point water was added until the remaining C and oil overflowed the flotation cell; this fraction was the middling product and the solids left in the cell were the tailings. All of the fractions were filtered, but the concentrates and the middling were also washed with alcohol to remove the oil. The fractions were then dried and weighed. If the concentrate fractions were large enough they were analyzed separately, otherwise some were combined prior to analysis. The analyses for all of the concentrates were combined as a composite concentrate to determine the overall grade and recovery.

A series of agglomeration tests was run to evaluate the effects of % solids, agitation rate, and grinding time. Increasing the solids content of the slurry to 40% resulted in poor separation of C from the residue. Agglomeration test results were also affected by the volume of slurry used and the number of oil additions. The one test in which a low-grade concentrate was cleaned by remixing it with water resulted in a concentrate that contained only 58% C at a recovery of 79%.

The number of C fractions recovered varied from 2 to 9, with an average of 5.5, depending on how much oil was used, how the oil was added, and the solids content of the slurry. An average of 4.8 fractions were analyzed. The first 1-4 fractions collected tended to be the cleanest and have the highest C grade. The individual concentrate fractions contained 51-82 C, 1.6-6.6 Fe, 0.7-6.2 Zn, and 0.3-1.6% Pb, and 75-520 ppm As and 39-247 ppm Cd. The average first concentrate fraction from each test contained 7.6% of the original sample weight and recovered 27.8% of the C at an average grade of 73.3%. The average first concentrate also contained 2.51 Fe, 1.43 Zn, and 0.51% Pb, and 150 ppm As and 65 ppm Cd. The average last concentrate fraction (or group of fractions) from each test contained 2.6% of the original sample weight and recovered 9.6% of the C at an average grade of 68.6%. The average last concentrate also contained 3.34 Fe, 2.42 Zn, and 0.65% Pb, and 196 ppm As and 113 ppm Cd.

The average composite concentrate from the tests shown in Table 6 contained 21% of the original sample weight and recovered 73.5% of the C at an average grade of 72.6%. The average composite concentrate also contained 2.74 Fe, 1.62 Zn, and 0.59% Pb, and 153 ppm As and 79 ppm Cd. Seven concentrate fractions were collected in test 0-17, which yielded the best C grade and recovery.

Statistical analysis of these agglomeration tests with castor oil indicated that the only moderately positive effect was the interaction between grinding time and pulp solids. Increased grinding and agitation had a slight tendency to reduce the C grade, while increased agitation and % solids had a slight tendency to increase the C recovery. At 1,100 rpm, an average of 139 g of castor oil/kg of residue was required to recover an average of

TABLE 6. OIL AGGLOMERATION RESULTS (CASTOR OIL)

Test	Grind Time (min)	Agitation Rate (rpm)	Pulp Solids (%)	Carbon Grade (%)	Carbon Recovery (%)
0-11 . .	30	2,200	10	69	70
0-12 . .	30	1,100	10	71	69
0-16 . .	30	2,200	20	69	75
0-17 . .	30	1,100	20	79	78
0-18 . .	5	2,200	10	73	74
0-19 . .	5	1,100	10	76	76
0-20 . .	5	2,200	20	74	77
0-21 . .	5	1,100	20	69	67

73% of the C at an average grade of 74%. At 2,200 rpm, this was reduced to about 106 g/kg to recover an average of 74% of the C at an average grade of 71%.

The two tests shown in Table 7 required an average of 206 g of kerosene/kg of residue to recover 78% of the C at an average grade of 72%. A similar test, run with fuel oil, required 221 g/kg of oil to recover 71% of the C at a grade of 81%. The C grades and recoveries for these last three tests may be elevated due to incomplete removal of the kerosene and fuel oil prior to analysis.

The good recoveries obtained on a larger scale indicated that the initial tests did not have enough agitation for good oil-carbon contact.

FLOTATION

Flotation has also been used to recover coal fines. The coal slurry is intensely mixed with an oil or other collector that selectively attaches to the coal particles. The slurry is then mixed with a frother. The frother, plus air introduced through the

TABLE 7. OIL AGGLOMERATION RESULTS (KEROSENE)

Test	Grind Time (min)	Agitation Rate (rpm)	Pulp Solids (%)	Carbon Grade (%)	Carbon Recovery (%)
0-22 . .	30	2,200	10	70	83
0-23 . .	30	2,200	10	75	80

agitator in the bottom of the flotation cell, creates a froth with the necessary properties to float the treated coal particles so they can be skimmed off the surface of the slurry (14). The two important benefits of flotation over agglomeration for residue treatment are the easy recovery of C in the froth and the use of less oil as a collector.

Bench-Scale Tests

Bench-scale froth flotation tests were conducted on representative portions of the composite residue sample D7C. A number of different oils and frothers were tried to determine which combination gave the best C grade and recovery. The results of these initial tests indicated that good C recoveries could be obtained while using much less oil than agglomeration. Carbon analyses on the flotation tailings were similar to, or lower than, those on agglomeration tailings, indicating better C recovery in the flotation concentrates.

A typical test used 150 or 260 g of residue ground in a small stainless steel rod mill at about 14% solids. The resulting slurry was washed out of the mill and transferred to a small PVC flotation cell where it was diluted to about 5.4% solids. The oil used as a collector was added to the cell and mixed with the slurry for a fixed time, then the same was done with the frother. Air was then injected through the agitator and the froth was collected by scraping it over the lip of the cell. When more than one concentrate was taken, the first one usually was the only one with a good C grade; these are the concentrates discussed below. The difference in C grade between consecutive concentrates was much greater than in the agglomeration tests.

Since castor oil, a convenient and relatively nontoxic reagent, worked well in the agglomeration tests, it was evaluated as a collector in C flotation. The first concentrates from these tests contained an average of 21.5% of the original sample weight and recovered 76.6% of the C at an average grade of 69.9%. The average concentrate also contained 3.0 Fe, 2.1 Zn, and 0.5% Pb, and 178 ppm As and 82 ppm Cd. The results for the individual tests are shown in Table 8.

Additional tests were run with fuel oil for comparison. The first concentrates from these tests contained an average of 20.1% of the original sample weight and recovered 71.4% of the C at an average grade of 69.4%. The average concentrate also contained 3.5 Fe, 2.3 Zn, and 0.6% Pb, and 216 ppm As and 87 ppm Cd. These results are given in Table 9.

Although one of the tests with fuel oil (F-8) had the highest C grade of all the flotation tests, the grades and recoveries for the fuel oil tests may be elevated due to incomplete removal of the fuel oil prior to analysis.

Since the initial tests with castor oil were successful, it was used as the collector in all subsequent tests. The initial tests used 3.2-6.41 g of castor oil/kg of ground residue and required 1.53-3.67 g of frother/kg of residue to produce the first concentrate. The initial tests recovered 1 or 2 concentrates. An effort was made to reduce reagent consumption while maintaining C grade and recovery. Since flotation tests on the retort residue using only frothers indicated that the cleanest concentrates were produced with pine oil, pine oil was used as the frother in all but one of the subsequent tests.

Four tests that used 0.87-0.90 g of castor oil/kg of residue required 1.82-2.04 g of frother/kg of residue for the first concentrates, which contained an average of 67% C at a recovery of 75.6%. In one of these tests, the castor oil was added to the rod

TABLE 8. FIRST FLOTATION CONCENTRATES PRODUCED WITH CASTOR OIL

Test	Wt %	C Grade (%)	C Recovery (%)	As (ppm)	Cd (ppm)	Fe (%)	Pb (%)	Zn (%)
F-1	20.8	74.7	76.9	141	77	2.36	0.38	1.86
F-2	20.7	69.7	74.7	201	91	3.20	0.58	2.15
F-3	19.2	73.7	70.7	110	70	2.01	0.28	1.85
F-4	21.3	66.4	75.8	204	81	3.16	0.58	2.05
F-5	25.5	64.8	85.0	235	90	4.19	0.71	2.47

TABLE 9. FIRST FLOTATION CONCENTRATES PRODUCED WITH FUEL OIL

Test	Wt %	C Grade (%)	C Recovery (%)	As (ppm)	Cd (ppm)	Fe (%)	Pb (%)	Zn (%)
F-6	15.0	64.8	55.3	166	85	2.77	0.52	1.87
F-7	19.6	67.3	71.7	231	94	3.88	0.74	2.47
F-8	22.0	78.7	81.6	168	70	2.94	0.57	2.05
F-11	23.8	66.9	76.8	299	98	4.23	0.76	2.85

mill to make sure it was thoroughly dispersed, resulting in a concentrate that contained 74.1% C at a recovery of 84.1%.

A series of 10 tests using 0.50-0.52 g/kg castor oil required only 0.79-1.31 g/kg pine oil for an adequate froth, but the C grade of the average concentrate decreased to 66.4% at a recovery of 70.9%. The average concentrate also contained 4.7 Fe, 2.3 Zn, and 0.7% Pb, and 270 ppm As and 66 ppm Cd. In this series of tests, the castor oil was always added to the rod mill except when the feed was preground to 100% minus 400 mesh. One of the tests with the oil added to the mill, run at 9% solids, yielded a concentrate with 73.2% C at a recovery of 76.8%.

In another test, the pine oil was mixed with the castor oil in a 2:1 volumetric ratio to reduce the viscosity of the castor oil before adding it to the rod mill. At an addition rate of 0.35 g/kg for the castor oil and 1.2 g/kg for the pine oil, this test used the smallest amount of collector and produced a first concentrate containing 68.1% C at a recovery of 63.6%.

Three samples of C concentrate produced with castor oil and pine oil from 260g of residue were wet-screened at 400 mesh. The plus 400 mesh fractions in these tests contained 46-52% of the concentrate sample. The C contents of the original concentrates were 71.2, 71.5, and 73.2%, while the plus 400 mesh fractions were 85.6, 77.7, and 80.3%, respectively, with recoveries of 60.2, 50.4, and 59.6% of what was in the original concentrate. The other analyses for the size fractions are given in Table 10. The plus 400 mesh fractions contained 12-18% of the As, 25-32% of the Cd, 20-24% of the Fe, 20-23% of the Pb, and 26-30% of the Zn that was in the original concentrate. Depending on how the flotation feed is ground, this may offer a method for recovering a significant fraction of the C as a relatively clean product without needing to leach it. The plus 400-mesh concentrate fractions will be subjected to the TCLP. The minus 400-mesh fractions will be leached in an attempt to reduce the Cd, Pb, and Zn levels, and characterized to determine whether the C can be separated from the phases containing As, Cd, Fe, and Pb.

Residue samples ground for standard and reduced times, as well as at higher solids content, are being separated into size fractions and analyzed. Bench-scale flotation tests are being run to evaluate the effect of solids content and particle size on concentrate grade. The first concentrate from each test is being screened at 400 mesh to determine the effect of the changes in grinding on the production of a premium concentrate by screening.

Large-Scale Tests

Approximately 18 kg of composite retort residue D7C was stage-ground in the small rod mill to 100% minus 400 mesh to provide feed for a series of large-scale flotation tests. About one-third of

TABLE 10. ANALYSIS OF CONCENTRATE SIZE FRACTIONS

Test	Fraction	As (ppm)	Cd (ppm)	Fe (%)	Pb (%)	Zn (%)
1 . .	+400	79	40	1.75	0.29	1.12
	-400	400	93	6.19	1.05	2.96
2 . .	+400	62	34	1.74	0.30	1.22
	-400	373	87	6.02	1.0	2.86
3 . .	+400	70	35	1.80	0.34	1.26
	-400	354	95	6.75	1.16	3.28

this sample was processed in an experimental flotation device. Both concentrate and tailing samples were taken on each of seven passes of the slurry through the device. Since X-ray fluorescence and C analyses of the samples indicated that little or no separation took place, the remainder of the used slurry and the rest of the ground sample were set aside until standard flotation cells were set up.

Three tests were run in a bank of 11-L flotation cells using approximately 6 kg of the minus 400-mesh retort residue per test. One cell was used to produce a rougher concentrate and two cells were used as scavengers, to produce the middling fraction. The conditioned slurry was pumped into the cells at about 3 L/min.

The first test used the leftover slurry from the experimental device test. Since reagents had already been added to this batch, only about 1 mL of mixed pine oil and castor oil was added. The low froth level in the cells resulted in the recovery of only 93 g of concentrate (C1). This concentrate was saved, and everything else was returned to the conditioner. More pine oil was added to improve the froth. This resulted in a heavy black froth from the first cell (880 g, C2), a brown froth from the third cell, and no indication of residual C floating on the tailings. The slurry remaining in the three cells at the end of the test was saved in separate containers for the next test.

The second test was similar to the first except that the feed was a fresh batch of ground retort residue plus the small amount of slurry left in the conditioner at the end of the first test. Each cell was filled with the slurry drained from that cell after the previous test, plus 1/2 mL of mixed pine oil and castor oil. The feed slurry was conditioned with approximately 0.93 g/kg of castor oil for 10 min. A total of about 1.4 g/kg of pine oil was required to produce an adequate froth. This test produced 1,024 g of concentrate (C3).

The third test used about 0.52 g/kg of castor oil that was added as a 1:1 mixture of castor oil and ethanol for better dispersion of the viscous castor oil. With this reduced addition of castor oil, only about 0.78 g/kg of pine oil was required to produce an adequate froth. This concentrate weighed 988 g (C4).

The concentrate analyses from the three large-scale tests are given in Table 11. Concentrate C2 is lower in Cd, Fe, and Zn than all of the concentrates from the bench-scale tests. Concentrates C2 and C4 are lower than the bench-scale average in As, Cd, Fe, Pb, and Zn content. The substantial difference between the first two concentrates indicates that the frother dosage has a significant impact on the quality of the concentrate.

Several tests have been run in the bench-scale flotation cell in an attempt to clean the concentrate produced in one of the large-scale tests. The best results were obtained with no additional reagents. The C content of concentrate C3 was upgraded from 64.4 to 72.5%, with a recovery of 72%. The cleaned concentrate also contained 4.67 Fe, 2.75 Zn, and 0.95% Pb, and 137 ppm As and 66 ppm Cd. While this is an improvement over the original concentrate, it is not as clean as the plus 400 mesh fractions of concentrates obtained in the bench-scale cell. Better results may be obtained by using more than one cleaning stage. Future large-scale tests will use reduced grinding times in addition to large-scale cleaning tests to optimize the production of high-grade concentrate.

TABLE 11. GRADE OF LARGE-SCALE CONCENTRATES

Conc	C (%)	As (ppm)	Cd (ppm)	Fe (%)	Pb (%)	Zn (%)
C1 . .	54.1	526	95	6.25	1.52	4.10
C2 . .	84.1	124	43	1.76	0.67	1.45
C3 . .	64.4	369	84	6.02	1.10	3.16
C4 . .	77.8	173	61	3.46	0.64	2.07

The large-scale middlings and tails will be used for flotation, gravity concentration, and magnetic separation tests.

CONCLUSIONS

Carbon can be recovered from horizontal retort zinc smelter residue by oil "agglomeration" if the high oil consumption and difficult separation could be tolerated. Although up to 78% of the C could be recovered at concentrate grades up to 79%, all of the concentrate fractions had to be combined to get this level of C recovery. Froth flotation is a more attractive alternative for C reclamation since it offers lower reagent consumption, easy separation, faster throughput with less equipment, and can yield C grades up to 84% and C recoveries up to 85%. The concentrate grade can be improved by cleaning, and the recovery may be improved by returning the scavenger product (middlings) to the rougher flotation. The flotation concentrates contain Cd and Pb and may require additional treatment to be removed from the site, depending upon the regulatory status of the site. They may find a use as a waste-derived fuel or process reductant at some of the larger sites.

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