



Characterization and batch testing of a secondary lead slag

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Synopsis

The emphasis of this paper is on the characterization and testing of the slag produced by a secondary lead refinery. This work forms part of a broader investigation aimed at reducing loss of valuable product from the process as well as minimizing the environmental impact of the process wastes. It was this work that led to a critical examination of the standard waste classification tests.

Characterization of the slag was carried out using a number of complementary techniques. In the broader context, the slag characterization aided in identifying process deficiencies and thus was a critical tool in suggesting potential for process optimization. For this study, the slag characterization provided a relatively comprehensive picture of the composition and properties of the slag, which facilitated understanding the behaviour of the slag under batch test conditions.

On the basis of quantity of hazardous components alone, the slag is hazardous according to South African Acceptable Risk Limits (ARL). However, when both the quantity and the leach potential of the hazardous components is taken into account, standard waste tests carried out by three independent agencies indicate that the slag should not be classified as hazardous according to local regulations. Also, according to United States Environmental Protection Agency (US EPA) limits, which are independent of the quantity of the waste, the slag would not be classified as hazardous.

The standard waste tests used by the independent agencies was the Toxicity Characteristic Leach Procedure (TCLP), a test which was developed by the US EPA to classify hazardous wastes. One of the requirements of this batch test is that it should be quick, simple to carry out and that the results should be reproducible. Previously, the applicability of the TCLP test to mineral processing and metallurgical wastes has been challenged on a number of points.

Additional testing of the slag was carried out using both the TCLP and the Synthetic Precipitation Leach Procedure (SPLP) recommended by the American National Mining Association as being more appropriate for mineral processing wastes. The particular physical and chemical characteristics of the secondary lead slag highlighted additional limitations of both the TCLP and SPLP tests as standard laboratory batch procedures.

Keywords: environmental protection, secondary lead processing, slag, leach testing, TCLP, SPLP, ARL, hazardous waste, batch tests

Background

This work focuses on the slag produced by a secondary lead smelter that operates in South

Africa. The major input of the plant is scrap automotive batteries, with a lesser amount of drosses. Some galena concentrate is also processed. Of the waste that is generated, the slag represents the largest quantity and is also the most costly, both economically and environmentally. It has thus been the major focus of this work.

This paper deals only with slag characterization and a critical examination of the standard waste classification tests in the light of the particular characteristics of this waste material. For further information on Waste Minimization through Process Optimization and Waste Modification see Lewis¹ and Lewis *et al.*².

Slag characterization

Elemental analysis of the slag

An elemental analysis of 46 slag samples was carried out using ICP. These analyses were carried out on the plant as part of the routine sampling programme. The 46 slag samples each came from a different batch and originated from three different furnaces as follows: 9 batches from the 20 ton furnace, 18 batches from the 10 ton furnace and 19 batches from the 7 ton furnace. The sampling procedure is as follows: a sample rod is inserted into the slag pan as the slag is tapped. The rod is then withdrawn from the pan and allowed to cool. It is then broken up with pestle and mortar and sieved. What passes through the sieve is thoroughly mixed and then a random sample of 0.2g is taken, acid digested and analysed using ICP.

The elements analysed for were Sn, Sb, Pb, Fe, S, Zn, As, Al, Ca and Na. The average mass per cent and standard deviation for all the elements analysed is given in Table I.

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Table I

Concentrations of elements in the slag

| Elements | Average concentration (mass %) | Standard Deviation |
|----------|--------------------------------|--------------------|
| Sn | 0.7 | 0.3 |
| Sb | 0.4 | 0.5 |
| Pb | 9.2 | 11.0 |
| Fe | 22.2 | 8.7 |
| S | 7.6 | 2.2 |
| Zn | 1.6 | 1.3 |
| As | 0.15 | 0.2 |
| Al | 1.2 | 5.3 |
| Ca | 1.3 | 0.3 |
| Na | 16.1 | 5.4 |

The analysis shows that, not only are there significant concentrations of the elements of interest, Pb and Zn, in the slag, the concentration of all elements is extremely variable. This is a reflection of the extremely erratic and unpredictable nature of the slag composition.

A breakdown including Si cannot be given since the analysis is carried out as part of routine plant procedure and Si is not analysed for on the plant. However, an independent analysis³ carried out on a different set of slag samples found the mass percentage of silicon to be 9.42%.

SEM-EDS analysis of the slag

A number of different slag samples were subjected to Scanning Electron Microscopy (SEM) using a backscatter detector at a magnification of between 1000x and 5000x in conjunction with Energy Dispersive Spectroscopy (EDS). The samples were not polished, as the intention was to examine the morphology of the different phases. The analysis of the chemistry was intended to be qualitative only. Given the extreme heterogeneity of the slag, this analysis can only be expected to provide a broad overview of the possible compounds that are likely to be present in a range of different slags.

A sample of some of the SEM pictures are attached in Appendix A. The bright white particle(s) in SEM 1, SEM 4 and SEM 6 were identified as elemental lead, occurring as prills approximately 2µm and smaller in diameter. It is also possible that the prills might be PbS. From the pictures, it is apparent that the prills are distributed widely throughout the slag matrix. This lead (or PbS) can originate either from PbO or PbSO₄ that has been reduced in the furnace. If it is pure lead, it could be from the elemental lead that is introduced into the furnace with the battery plates.

SEM 1 shows an iron oxide matrix (light grey area) and a dark grey area, which was identified as containing sodium and oxygen. This is a surprising result, as the sodium in the slag is expected to be mostly in the form of sodium sulphide and bound up in silicate matrices.

SEM 2 and SEM 3 show octahedral crystals, which were identified as iron oxide spinels. Columnar blocks are iron sulphides. Sodium sulphide is also present as amorphous, dark grey areas. SEM 3 also shows plate crystals of pure tin. SEM 5 shows zinc present as zinc sulphide in the predominantly grey area.

The presence of iron sulphide and sodium sulphide in the

slag is consistent with expected furnace operating conditions. However, the presence of iron and sodium oxides in the slag could suggest that incomplete reduction is occurring in the furnace. Additional evidence for incomplete reduction would be the absence of elemental carbon and the presence of sodium sulphates and lead sulphides.

The trends identified by the SEM-EDS analysis were confirmed by a number of duplicate analyses on different slag samples.

An independent analysis³ carried out on a different set of slag samples used a polished section for SEM-EDS. That analysis identified the sodium in the sample as being part of amorphous Na-Fe sulphides as well as Na-Al silicates. This finding is more in keeping with what would be expected in the slag. The lead in the slag was identified as being mostly in the form of elemental lead, with a small amount in the form of PbS.

XRD analysis

X-ray diffraction (XRD) analysis was carried out on 2g samples from different furnaces in order to obtain qualitative data about the compounds present. Because of the extreme variability of the slag, this analysis cannot be considered to be conclusive. In general, there were significant amounts of X-ray amorphous slag matrix phases present. The major purpose of carrying out the analysis was to gain some information as to the forms in which Pb, Zn and As occur in the slag as this would provide information on their leachability, an important factor in the TCLP test.

Although not all likely compounds of Pb, Zn and As can be detected, the lead compound that appeared most strongly was anglesite (PbSO₄). Zinc was found present as wurtzite (ZnS), zinc hydroxide (Zn(OH)₂) and in a sodium zinc silicate. Arsenic was observed in the form of a sodium cadmium arsenate.

Slag testing

According to South African regulations, the slag would be classified as hazardous on the basis of its composition alone. The Estimated Environmental Concentration (EEC) of all three hazardous compounds greatly exceeds the South African Acceptable Risk Limit (ARL). See Table II for results and Appendix B (a) for a sample calculation.

However, when the standard waste classification tests were applied to the waste (as recommended⁴), the waste no longer qualified as hazardous. Three independent agencies carried out standard waste tests on the slag. The test used

Table II

Expected Environmental Concentrations of hazardous components in the slag based on slag composition compared to South African Acceptable Risk Limits

| Elements | EEC (ppm) | SA ARL ⁴ (ppm) |
|----------|-----------|---------------------------|
| Pb | 62 744 | 0.1 |
| Zn | 10 912 | 0.7 |
| As | 1023 | 4.3 |

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was the Toxicity Characteristic Leach Procedure (TCLP). According to United States Environmental Protection Agency (US EPA) limits, the slag would also not be classified as hazardous. The results of the waste tests for South African regulations are detailed in Table III, with a sample calculation in Appendix B (b). The waste test results for the United States regulations are detailed in Table IV.

Applicability of the TCLP to minerals processing wastes

The standard waste test used in this case was the TCLP, a test that was developed by the US EPA to classify hazardous wastes. Previously, the applicability of the TCLP test to mineral processing and metallurgical wastes has been challenged on a number of points⁶. The leachant used in the TCLP test is acetic acid. This choice is based on a co-disposal assumption, acetic acid being used to simulate the organic acid generated by municipal waste. The fact is that mineral processing wastes are not generally co-disposed but typically are treated in monofills that are neutral or alkaline in nature. Consequently, the Synthetic Precipitation Leach Procedure (SPLP) has been recommended by the American National Mining Association as being more appropriate for mineral processing wastes. The SPLP prescribes a leachant that is a combination of H₂SO₄ and H₂NO₃, a mixture that is intended to simulate the composition of acid rain⁷.

The TCLP has also been challenged on the basis of the particle size reduction requirement for the test, as this does not reflect conditions in which mineral processing wastes are generally managed. Mineral processing wastes are usually rocklike, monolithic structures, whose form means that leaching is minimized.

An additional problem with the TCLP for certain wastes is that the Acid Neutralizing Capacity (ANC) of the waste can

neutralize the acidity of the testing leachant, rendering true assessment of the leaching potential impractical⁸. This is particularly true for the assessment of the longer term leaching potential after the ANC of the waste is exhausted. Also, the elevated pH conditions can cause the leaching of some amphoteric heavy metals to occur in a highly alkaline environment instead.

Specific applicability of the TCLP and SPLP to the lead slag

A series of experiments was carried out in order to explore further the applicability of the TCLP and SPLP to this waste as well as to examine some of the potential difficulties encountered in implementing the test in the laboratory.

Sampling method

A single 2-ton slag pan from the 20 ton furnace was allowed to cool and then manually broken up into blocks of approximately 1–10 kg. Approximately ten of these blocks were selected randomly from different locations in the pile of broken-up slag to make up a sub-sample of approximately 20 kg. The 20 kg sub sample was crushed in a jaw crusher and sieved through an 8 mm sieve. Further sub samples were then collected randomly through dip sampling from the container holding the sieved slag.

Experimental Methods

Ten TCLP tests and ten SPLP tests were carried out on the same 20 kg sub sample of slag. The TCLP procedure followed was that specified in the US EPA Federal Regulations⁵, the SPLP procedure being that specified by Environment Canada⁷.

Filterability problems

For both tests, the first problem was encountered at the stage where the leachate is to be filtered from the solid residue. Because of the extremely fine and coagulating nature of the solid residue, the prescribed filtration step was impossible to carry out due to blinding of the filter medium. Consequently, a representative sample of the contents of the TCLP flask (extract + residue) were centrifuged (8000 rpm for 30 min) in order to make it possible to carry out the subsequent filtration of the samples. After centrifuging, the samples were filtered, in accordance with the standard procedure.

Analytical problems

The second problem was encountered with the analysis of the filtered extract, as this was a dark green fluid, still containing particles in suspension, despite the 0.45µm filtration step. The sludge-like character of the extracts meant that they were impossible to analyse directly using conventional Atomic Absorption Spectroscopy (AAS) techniques. However, it was possible to analyse them directly using Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) techniques. Consequently, two sets of analyses were carried out on each sample: direct ICP–MS analysis and AAS analysis after the samples had been acid digested as specified in the US EPA procedure⁵.

The chemical composition of the slag

One of the shortfalls of the TCLP test is the inappropriate

Table III
Independent TCLP tests and South African regulatory limits

| Elements | EEC (ppm) | | | SA ARL ⁴ (ppm) |
|----------|--------------------|--------------------|--------------------|------------------------------|
| | Agency A Oct-97 | Agency B Jan-98 | Agency C Sep-98 | |
| Pb | 0.005 | 0.010 | 0.003 | 0.1 |
| Zn | 0.095 | 0.014 | 0.009 | 0.7 |
| As | 0.023 | 0.0004 | not tested | 0.43 |

Table IV
Independent TCLP tests and United States regulatory limits

| Elements | Concentration (ppm) | | | |
|----------------------|---------------------|--------------------|--------------------|-------------------------------|
| | Agency A Oct-97 | Agency B Jan-98 | Agency C Sep-98 | US EPA limits ⁵ |
| Concentrations (ppm) | | | | |
| Pb | 0.34 | 0.71 | 0.2 | 5 |
| Zn | 7.0 | 1.0 | 0.65 | not defined |
| As | 1.7 | 0.03 | not tested | 5 |

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nature of the prescribed leachant. Not only is acetic acid unlikely to be encountered in the monofills in which mineral processing waste is normally treated, but lead forms a stable complex with acetic acid. This should be apparent in high values of lead in the TCLP test results. These results would be an artefact of the test conditions alone and not an accurate reflection of the levels of lead that will be leached out in the field.

In addition, this slag is known to be highly alkaline, which will not only affect the pH during the test, but will also increase the quantities of lead recovered in the extract due to the amphoteric nature of lead solubility.

In a landfill, as the acid neutralizing capacity of the waste is consumed over time, the final pH of the leachant will drop into the region in which the solubility of lead undergoes a minimum. Eventually, under acidic conditions, the pH might well drop into the region where the solubility of lead increases again⁹. See Figure 1. Ultimately, the quantity of lead released into solution is a strong function of *both* the type of leachant and the residual acid neutralizing capacity of the waste over time.

Results

The results of the TCLP tests are presented in Table V and the results of the SPLP tests are presented in Table VI.

These results were analysed statistically to determine whether or not the AAS and the ICP-MS results could be pooled into a single sample. It was found that there was no statistical difference at the 95% confidence interval between the means for the lead readings. However, the statistical tests showed that the zinc readings differed significantly and could not be pooled. Due to a history of unreliability in zinc readings from the ICP-MS analysis, the AAS readings were taken to be more representative of the true zinc values. A summary of all the tests to date carried out on the slag is presented in Table VII with reference to South African regulatory limits and Table VIII with reference to United States regulatory limits. The results generated in this study are labelled UCT TCLP and UCT SPLP respectively.

Discussion

The quantities of lead, zinc and arsenic leached out in both tests are considerably higher than in any previous tests. For the UCT TCLP and UCT SPLP test, results obtained for lead exceed the South African Acceptable Risk Limit although the

results for zinc and arsenic fall below the risk limit. Nonetheless, this slag would be classified in South Africa as hazardous on the basis of the lead result alone.

Table V

TCLP results

| Sample no. | pH | | Concentrations in TCLP extract samples (ppm) | | | | |
|------------------|-------------|--------------|--|-------------|----------------------|-------------|--------------|
| | | | From AAS readings | | From ICP-MS readings | | |
| | Start | End | Pb | Zn | Pb | Zn | As |
| 1 | 3.78 | 10.65 | 94.8 | 7.10 | 79.9 | 5.26 | 24.5 |
| 3 | 4.08 | 10.82 | 120.7 | 6.05 | 68.1 | 2.39 | 23.1 |
| 4 | 4.18 | 10.41 | 100.3 | 5.17 | 77.9 | 3.24 | 25.4 |
| 5 | 3.90 | 10.63 | 106.4 | 8.68 | 81.9 | 7.88 | 33.7 |
| 6 | 4.06 | 10.64 | 153.8 | 7.47 | 132 | 5.69 | 23.5 |
| 8 | 3.84 | 10.51 | 90.1 | 7.25 | 93.9 | 5.72 | 25.0 |
| 9 | 3.67 | 10.58 | 96.3 | 7.73 | 82.2 | 6.09 | 25.5 |
| 10 | 3.90 | 10.81 | 120.1 | 6.27 | 118 | 5.06 | 27.8 |
| Average | 3.91 | 10.61 | 110.3 | 6.96 | 95.94 | 5.39 | 26.01 |
| STD. Dev. | 0.17 | 0.13 | 20.9 | 1.10 | 23.38 | 1.63 | 3.28 |

Table VI

SPLP results

| Sample no. | pH | | Concentrations in SPLP extract samples (ppm) | | | | |
|------------------|--------------|--------------|--|-------------|----------------------|-------------|--------------|
| | | | From AAS readings | | From ICP-MS readings | | |
| | Start | End | Pb | Zn | Pb | Zn | As |
| 1 | 11.89 | 12.51 | 44.1 | 3.87 | 38.7 | 2.08 | 33.7 |
| 2 | 11.87 | 12.48 | 212.3 | 9.10 | 126 | 5.44 | 26.5 |
| 3 | 11.90 | 12.50 | 97.6 | 15.90 | 75.1 | 14.7 | 36.7 |
| 4 | 12.07 | 12.52 | 52.1 | 3.31 | 39.5 | 1.02 | 30.3 |
| 5 | 11.74 | 12.49 | 153.4 | 6.32 | 91.2 | 4.52 | 33.5 |
| 6 | 11.70 | 12.49 | 117.7 | 10.04 | 138 | 7.90 | 27.6 |
| 7 | 11.53 | 12.55 | 61.5 | 2.90 | 58.7 | 1.74 | 34.4 |
| 8 | 11.63 | 12.55 | 58.2 | 2.60 | 36.9 | 1.52 | 30.6 |
| 9 | 12.06 | 12.57 | 109.5 | 6.06 | 79.1 | 4.88 | 27.1 |
| 10 | 11.76 | 12.54 | 187.4 | 18.05 | 119 | 14.2 | 26.5 |
| Average | 11.82 | 12.52 | 109.4 | 7.82 | 80.22 | 5.80 | 30.69 |
| STD. Dev. | 0.18 | 0.03 | 58.9 | 5.47 | 37.72 | 5.04 | 3.72 |

Table VII

Summary of all TCLP and SPLP tests carried out to date with reference to South African regulatory limits

| Elements | EEC (ppm) | | | | | SA ARL ⁴ (ppm) |
|----------|-------------|-------------|-------------|--------------------|-------------|---------------------------|
| | Agency A | Agency B | Agency C | UCT | UCT | |
| | TCLP Oct-97 | TCLP Jan-98 | TCLP Sep-98 | TCLP Dec-98 | SPLP Dec-98 | |
| Pb | 0.005 | 0.010 | 0.003 | 1.407* | 1.293 | 0.1 |
| Zn | 0.095 | 0.014 | 0.009 | 0.095 ^Δ | 0.107 | 0.7 |
| As | 0.023 | 0.0004 | not tested | 0.355 | 0.355 | 0.43 |

* Calculated from average for pooled samples

Δ Calculated from AAS readings

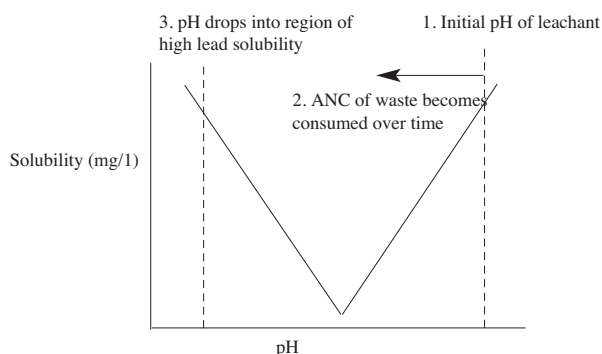


Figure 1—Schematic representation of amphoteric heavy metal solubility

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Table VIII

Summary of all TCLP and SPLP tests carried out to date with reference to US EPA regulatory limits

| Elements | Concentration (ppm) | | | | | |
|----------|---------------------|----------------|----------------|-------------------|----------------|-------------------------------|
| | Agency A | Agency B | Agency C | UCT | UCT | US EPA ⁵ limits |
| | TCLP Oct-97 | TCLP Jan-98 | TCLP Sep-98 | TCLP Dec-98 | SPLP Dec-98 | |
| Pb | 0.34 | 0.71 | 0.2 | 103.12* | 94.81 | 5 |
| Zn | 7.0 | 1.0 | 0.65 | 6.96 ^Δ | 7.82 | Not defined |
| As | 1.7 | 0.03 | not tested | 26.01 | 30.69 | 5 |

• Average for pooled samples

Δ AAS readings

The UCT TCLP and UCT SPLP results exceed the US EPA limits for both lead and arsenic. Contrary to expectations, even the SPLP test, with its supposedly less aggressive leachant, produces leachate concentrations far in excess of the regulatory limits. The lead concentration determined by the SPLP test is also only slightly less than that determined by the TCLP test. A much greater difference in the lead concentrations was expected due to the formation of a soluble lead acetate complex during the TCLP extraction. For zinc and arsenic, the SPLP test produced *greater* concentrations than the TCLP test.

These high concentrations of contaminants can partially be accounted for by the high pH values encountered during both the TCLP and the SPLP tests. The final pH of all the tests was never less than 10.4. For the TCLP tests, the average final pH was 10.61 and for the SPLP tests it was 12.52. At these alkaline pH's, the amphoteric nature of the lead and zinc compounds becomes a significant factor. Arsenic also exhibits amphoteric behaviour at pHs below 1 and above 8.

A second reason for the high concentrations of contaminants lies with the nature of the analytical procedure for the test. It is believed that previous analyses were carried out directly on the undigested TCLP extracts. This would significantly alter the results obtained.

Conclusions

Slag characterization

Both the ICP and SEM-EDS analyses confirm the highly erratic and heterogeneous nature of the slag composition. The presence of the toxic compounds lead; zinc and arsenic were also confirmed. These occur in the form of elemental lead, anglesite, zinc sulphide, zinc hydroxide, zinc silicates and sodium cadmium arsenate.

TCLP and SPLP tests

The applicability of the TCLP test to mineral processing and metallurgical wastes has previously been challenged on a number of points, including the nature of the leachant and the requirement for particle size reduction.

In addition, for this slag, the highly alkaline environments encountered in the batch tests are not

representative of conditions in the field, as the acid neutralizing capacity of the slag will be depleted over time. Also, the elevated pH conditions can cause the leaching of some amphoteric heavy metals to occur in alkaline regions and thus skew the batch test results.

The significant differences in the results of the UCT TCLP and UCT SPLP tests compared to previous tests is ascribed to the nature of the TCLP procedure itself. One of the requirements of this batch test is that it should be *quick, simple to carry out* and that the results should be *reproducible*. It is presumed that, due to analytical and filterability problems, previous analyses were carried out on inaccurately prepared samples, thereby leading to incorrect results. From previous test work carried out at this laboratory, it is known that, if the TCLP 'green sludge' extract is analysed directly using AAS techniques, the resultant metal concentrations will be much lower than if the 'green sludge' is correctly digested before analysis. These results highlight some of the important drawbacks of the TCLP test (for this slag)—that it is time-consuming, complicated to carry out and that the results are not reproducible.

In addition to the complications at laboratory level, the TCLP and SPLP tests are of questionable value for this slag due to its high acid neutralization capacity and specific chemical composition. The high pH values encountered during both tests means that the amphoteric nature of the lead, zinc and arsenic compounds would be a significant factor.

Closure

Laboratory batch extraction tests, such as the TCLP, are widely used to classify industrial solid wastes destined for disposal in landfills. Whilst the ease and speed of such tests makes their use an attractive option, it is also clear that the physical and chemical characteristics of the waste can render the tests meaningless. In addition, the physical and chemical mechanisms dominating in such tests do not bear much resemblance to those expected in a landfill situation. This makes the meaningfulness of the TCLP test highly dependent on the type of waste¹⁰.

It has been recognized that there is need for a more systematic approach to allow testing of a wide variety of material in a wide variety of contexts¹¹, and consequently a more fundamental understanding of factors involved in various tests and protocols has begun to emerge. This involves both a systematic approach to laboratory waste testing as well as equally rigorous and systematic tools to interpret the data.

Ultimately, the aim of meaningful waste testing methods should be the generation of leach data that can be interpreted in such a way that the potential leachate generation behaviour in a disposal scenario can be adequately forecast.

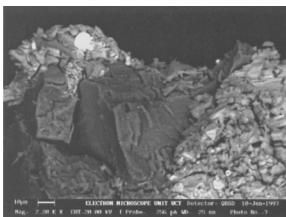
Acknowledgements

Grateful acknowledgements are due to Fry's Metals for their sponsorship of this project; Dane Gerneke of the Electron Microscopy Unit at UCT for his assistance and students Alex Pehlken, Timo Hardimann and Craig Beautement for their contributions to this study.

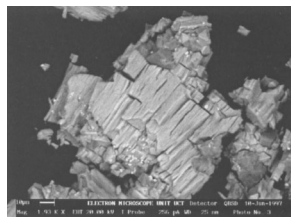
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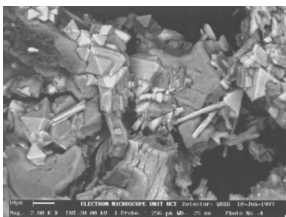
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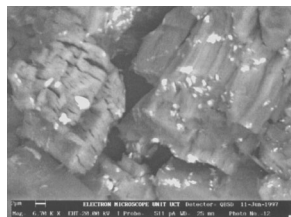
SEM 1



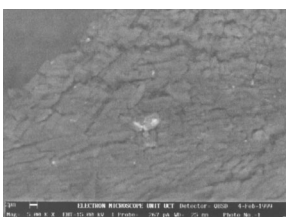
SEM 2



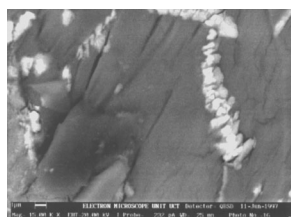
SEM 3



SEM 4



SEM 5



SEM 6

Appendix A—SEM pictures

- (a) based on mass % of hazardous component in the slag

Slag production: 12 400 tons slag / annum =
 $1.03 \cdot 10^9$ g slag/month

Pb: 9.2 mass % = $9.6 \cdot 10^7$ g/ha/month * 0.66
 (factor specified in⁴)/1000 (to convert to ppm) =
62 744 ppm

- (b) based on leachable portion of hazardous component

Slag production: 12 400 tons slag / annum =
 $1.03 \cdot 10^9$ g slag/month

TCLP result for Pb: 0.34 ppm

i.e. = 0.34 mg Pb in $1 \cdot 10^6$ mg H₂O * 2000 mg
 H₂O/100g slag (quantities used in TCLP
 test)

= $6.8 \cdot 10^{-6}$ mg Pb/g slag * $1.03 \cdot 10^9$ g

slag/ha/month / 1000 (to convert to g Pb)

= 7.03 g Pb/ha/month * 0.66 (factor specified
 in⁴) /1000 (to convert to ppm)

= 0.005 ppm

Appendix B—Calculation of South African Estimated Environmental Concentrations (EEF)