

BACTERIAL LEACHING OF Pb -METALLURGICAL WASTES

Received – Prispjelo: 2010-03-12

Accepted – Prihvaćeno: 2010-09-25

Preliminary Note – Prethodno priopćenje

The aim of this paper is verification of application of bacterial leaching and calcination to recover heavy metals from metallurgical wastes - matte from metallurgical plant Kovohute Pribram. For bacterial leaching a pure bacterial culture of *Acidithiobacillus ferrooxidans* was used. For a verification test an original sample of matte and matte from 2004 year were used. This paper further shows changes in the samples after bacterial leaching and after calcination. The paper results imply that the samples in question may be used as pigments.

Key words: Pb-metallurgical wastes, heavy metals, bacterial leaching, calcination

Bakterijsko izluživanje olovnog metalurškog otpada. Cilj ovog rada je potvrđivanje primjene bakterijskog izluživanja i kalcinacije za oporabu teških metala iz metalurških otpada – sulfida teških metala i željeza (eng. *matte*) iz metalurškog postrojenja Kovohute Pribram. Za izluživanje je potrebna bakterijska kultura *Acidithiobacillus ferrooxidans*. Za ispitivanje je korišten originalnu uzorak sulfida teških metala i željeza i uzorak sulfida teških metala i željeza iz 2004. godine. U ovom radu pokazane su promjene na uzorku nakon bakterijskog izluživanja i kalcinacije. Iz rezultata slijedi da se uzorci mogu koristiti kao pigmenti.

Ključne riječi: olovni metalurški otpad, teški metali, bakterijsko izluživanje, kalcinacija

INTRODUCTION

Some of the main objectives of the raw material policy, in order to reach the level of the countries of the European Union, are a lower exploitation of non-renewable raw material sources by their complex utilization, higher usage of secondary raw materials and recycling.

Lead waste recycling is a significant environmental problem. These are primarily products of the pyrometallurgical production of lead - process waste – slag and matte. With regard to the complex raw material processing, a future growth in such wastes can be expected.

It is possible to process lead waste by melting in boilers, in drum, hearth, blast and electric furnaces, etc. In the course of melting, the produce are crude or commercially useful lead (or lead alloy), slag, fly ashes and matte.

This technology was developed by a German firm VARTA (Germany); it is in successful operation in Germany, Sweden, Belgium, Czech (Kovohute Pribram) and also other countries are considering its implementation. The process lies in the processing of complete accumulators (devoid of electrolyte, i.e. aqueous solution of H₂SO₄, lead fouled) with coke and fluxing agent in a blast furnace. Burning of coke and other charge organic components reduces the metal fraction of the charge, and the lead breaks through a bottom outlet of the furnace. Slag and matte are periodically tapped; matte is a

product of charge desulphurization. Matte is heavier than slag and solidifies separately in the bottom part of the metal mould, it is separated mechanically. [1]

MATERIALS AND METHODS

The mineralogical composition of the analysed samples was determined by an X-ray diffraction analysis. Measurements were carried out at the URD-6 device (Seifert Roentgen (Freiberger Praezissionsmechanik)) in the laboratories of the Geological Engineering Institute at VSB - TU Ostrava.

The X-ray diffraction analysis identified the following mineralogical composition of the matte: akermanite (1,96 %), augite (5,90 %), galenite (0,61 %), maghemite (2,31 %), magnetite (22,55 %), albite (5,43 %), troilite (59,22 %), antimony (0,89 %), gehlenite (1,77 %) and lead (1,36 %).

For the bacterial leaching testwork a 10-litre airlift glass bioreactor patterned on the research of Deutsche Montan Technologie Company – Essen (Bayer, 1988) was used [2]. After sterilization of the reactor, the prepared samples of Pb-waste were placed in it together with the medium 9K without FeSO₄. After one hour of mixing and homogenising of the suspension, 1,000 ml of the pure bacterial culture *Acidithiobacillus ferrooxidans* was introduced into the reactor. The bioreactor was connected to an aquarium water aerator, which supplied the reactor with air. The air was cleaned in washers in 1 M H₂SO₄ solution to have more moisture and to remove airborne bac-

P. Fecko, I. Janakova, E. Pertile, E. Kulova, Institute of Environmental Engineering, VSB-Technical University of Ostrava, Ostrava, Czech Republic

teria. Mixing of 5 % suspension was done by air. The value of pH was measured by a laboratory pH-meter "RADELKIS" and the pH was kept at the optimal value of 1,8 – 2 during the whole experiment (28 days). The temperature was kept in the range of 26 - 30 °C during the whole experiment. After leaching the suspension was filtered on a Buchner funnel. The filter cake was washed in 100 ml of 1M HCl and in 200 ml distilled water before the determination of heavy metals. [3-12]

RESULTS AND DISCUSSION

Based on bacterial leaching the following results were obtained - See Tables 1 and 2.

Table 1 Results of bacterial leaching of matte – original sample (determined by an X-ray fluorescence method)

| Leaching time / % | Input | Week 1 | Week 2 | Week 3 | Week 4 | |
|-------------------|-------|--------|--------|--------|--------|-----|
| Content | Pb | 17 | 17 | 16 | 15 | 13 |
| | Zn | 0,24 | 0,1 | 0,1 | 0,1 | 0,1 |
| | Cu | 0,16 | 0,12 | 0,12 | 0,11 | 0,1 |
| | Fe | 56 | 39 | 37 | 35 | 34 |
| Recovery | Pb | 0 | 1 | 7 | 13 | 24 |
| | Zn | 0 | 58 | 58 | 58 | 58 |
| | Cu | 0 | 25 | 25 | 31 | 38 |
| | Fe | 0 | 30 | 34 | 38 | 39 |

Table 2 Results of bacterial leaching of matte – new sample (determined by an X-ray fluorescence method)

| Leaching time / % | Input | Week 1 | Week 2 | Week 3 | Week 4 | |
|-------------------|-------|--------|--------|--------|--------|------|
| Content | Pb | 11 | 10 | 10 | 10 | 9 |
| | Zn | 1 | 0,92 | 0,79 | 0,75 | 0,6 |
| | Cu | 0,27 | 0,26 | 0,25 | 0,24 | 0,23 |
| | Fe | 46 | 45 | 44 | 42 | 40 |
| Recovery | Pb | 0 | 6 | 10 | 13 | 18 |
| | Zn | 0 | 8 | 21 | 25 | 40 |
| | Cu | 0 | 4 | 7 | 11 | 15 |
| | Fe | 0 | 4 | 4 | 9 | 13 |

It is apparent from the bacterial leaching results with the pure bacterial culture of *Acidithiobacillus ferrooxidans* on a matte sample, labelled as the original sample, that the recovery of Pb is very low. Applying this technology, after one-month leaching it is possible to leach only approximately 24 % of Pb, the recovery of Zn is about 60 % and other monitored elements (Cu and Fe) leach up to 40 %. Figures 1 and 2 show the character of the original sample of matte prior to and post its bacterial leaching.

On the grounds of the experimental research it was confirmed that at pH value higher than 2, crusts are formed which are made up by predominant jarosite to

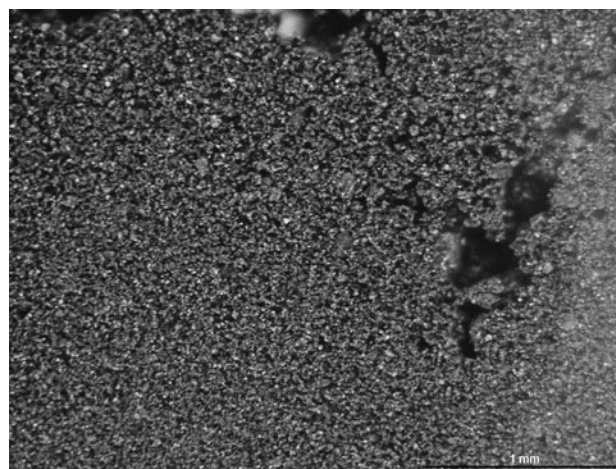


Figure 1 Matte-original sample (using a Zeiss NU-2 microscope)

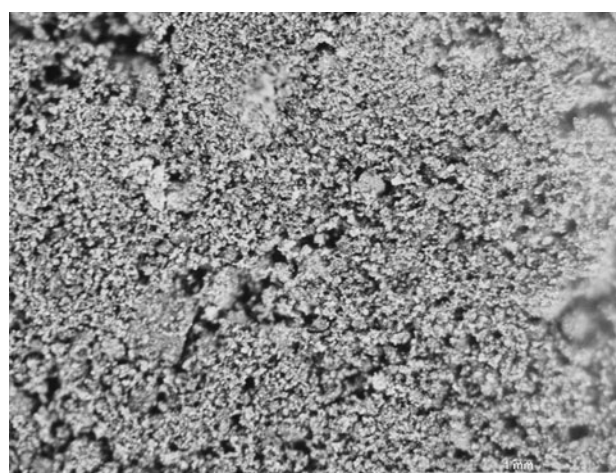


Figure 2 Matte-original sample after bacterial leaching (using a Zeiss NU-2 microscope)

which bacteria combine in great quantities. The figures imply that post bacterial leaching, it is possible to identify deposited mineral salts on the sample, which appear during bacterial leaching – especially the salts of jarosite.

The results of bacterial leaching with the new matte sample, sampled in 2004, imply that after the application of *Acidithiobacillus ferrooxidans* bacteria, from the new matte sample it is possible to extract approximately 18 % of Pb, 40 % of Zn and minimum of Cu and Fe. Comparing the results of bacterial leaching of both samples, it is possible to say that the results are similar, and that the application of bacterial leaching does not bring any positive results as the recovery of matte (both original and new) is considerably low. Comparing the character of the matte sample prior to and post leaching (Figures 3 and 4), it is noticeable that in case of the new sample it is not possible to observe such significant formation of salts as it was in case of the original matte. The new sample is worse extractable, which is confirmed by chemical analyses results that are better in case of the original matte sample.

Calcination is a process of annealing at high temperatures. The input samples (i.e. new and original matte) as well as all the samples post bacterial leaching were

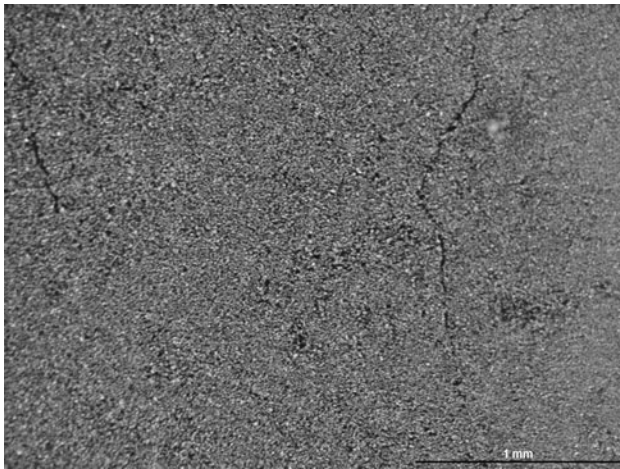


Figure 3 Matte – new sample (using a Zeiss NU-2 microscope)

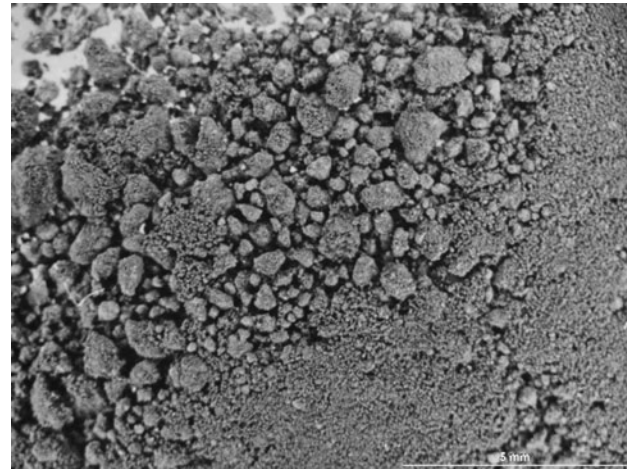


Figure 5 Matte – original sample after calcinations (using a Zeiss NU-2 microscope)

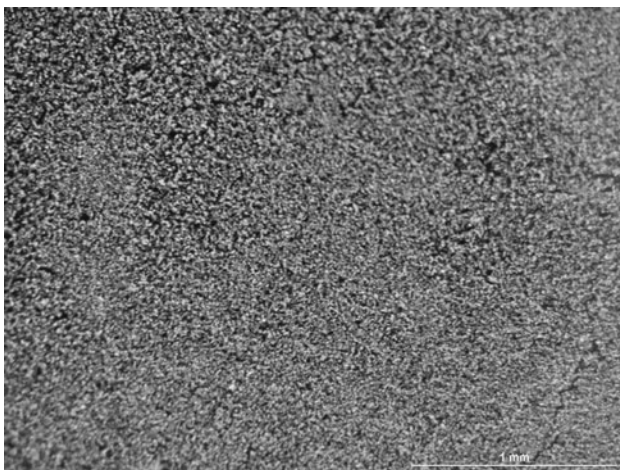


Figure 4 Matte – new sample after bacterial leaching (using a Zeiss NU-2 microscope)



Figure 6 Matte – original sample after bacterial leaching and calcinations (using a Zeiss NU-2 microscope)

subjected to calcination in a calcining furnace at the temperature of 650 °C for the period of 2,5 hours.

The calcination was implemented in order to produce mineral pigments and also it was very interesting to observe how the character of the individual samples change prior to and post calcination.

The chemical analyses results, stated in Table 3, imply that post calcination the fraction of monitored heavy metals grows (i.e. Pb, Cu, Zn and Fe) in the matte and there is no difference if it is the original sample or the sample post bacterial leaching.

Figures 5, 6, 7 and 8 state the character of all the samples after calcination.

Table 3 Heavy metal fraction (determined by an X-ray fluorescence method)

| Sample | Content / % | | | |
|---|-------------|------|------|----|
| | Pb | Zn | Cu | Fe |
| Matte – original sample | 20 | 0,13 | 0,1 | 36 |
| Matte – new sample | 4 | 0,1 | 0,1 | 32 |
| Matte –original – post bacterial leaching | 29 | 0,13 | 0,12 | 44 |
| Matte –new – post bacterial leaching | 12 | 0,58 | 0,24 | 43 |

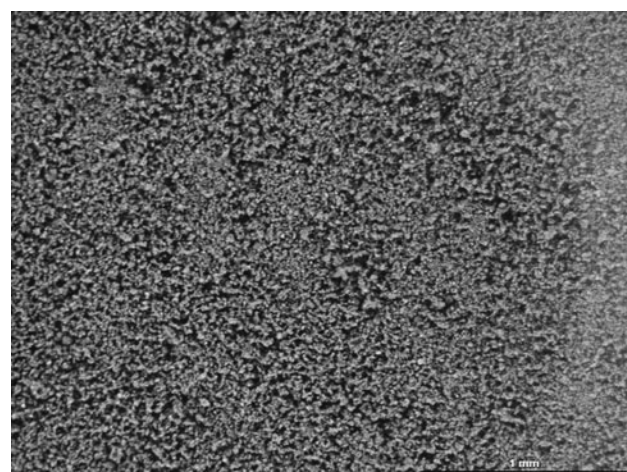


Figure 7 Matte – new sample after calcinations (using a Zeiss NU-2 microscope)

When concentrating on the colour change of the individual samples in Figures 5 – 8 it is clear that post the application of calcination it is possible to observe colour changes in all the samples, which are brick-red to brown. Among the individual samples, no significant changes are noticeable, but it is possible to see changes post bacterial leaching where under the microscope it is

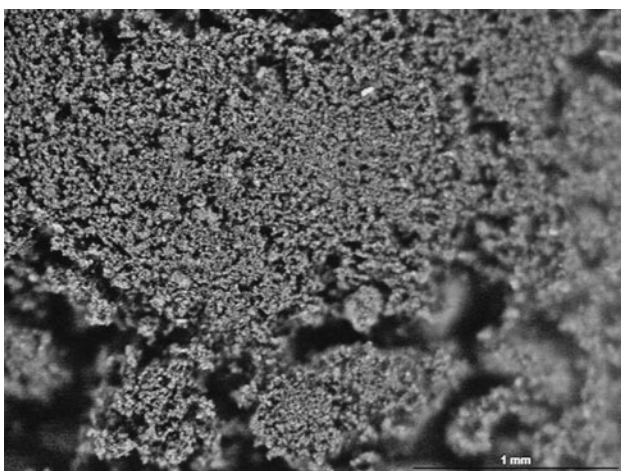


Figure 8 Matte – new sample after bacterial leaching and calcinations (using a Zeiss NU-2 microscope)

possible to identify rock gypsum needles. If this waste should be used as colour agents it would be necessary to carry out staining tests, e.g. with concretes, and to carry out extractability and stability tests with these concretes. On the grounds of the afore stated, it would be possible to decide whether their application is possible.

Matte – original sample: Troilite prevails over magnetite. There are traces of metallic lead. The record is indicative of the presence of a large amount of amorphous components.

Matte – new sample: Troilite dominates over magnetite, fayalite and wustite. There are traces of lead. The presence of amorphous components is not apparent.

Matte – original sample post bacterial leaching: Jarosite slightly prevails over troilite and magnetite. There is considerably little anglesite and galenite. There are traces of other non-identifiable phases (perovskite type phase).

Matte – new sample post bacterial leaching: Troilite prevails over magnetite, wustite and anglesite. There are traces of akermanite. Other trace non-identifiable phases and obviously also amorphous components are present.

Matte – original sample post calcination: Hematite – 81,3 % prevails over anglesite – 18,7 %.

Matte – new sample post calcination: Hematite – 84,5 %, anglesite – 8.8 %, anhydride 5,6 %

Matte – original sample post bacterial leaching and calcination: Hematite – 79,5 %, anglesite – 20,5 %.

Matte – new sample post bacterial leaching and calcination: Hematite – 85,8 %, anglesite – 14,2 %.

CONCLUSION

The X-ray analyses imply that after the application of bacterial leaching, the original samples contain typi-

cal minerals arising in connection with bacterial leaching, mainly rock gypsum and jarosite.

On the ground of research it was confirmed that the optimal pH value for bacterial leaching in the conditions of the laboratory of the Institute of Environmental Engineering, stated by Beyer [2], must not exceed the pH value range from 1,8 to 2,0. Raising the pH value, crusts of jarosite are clearly identified, which are undesirable for the subsequent process of calcination and there is also a deceleration in the process of bacterial leaching.

The application of calcination proved that all the samples with or without the application of bacterial leaching or post the application of bacterial leaching predominantly contain the minerals of hematite, in a high concentration over 80 %, and therefore it is possible to say that the samples can be used as colour agents or pigments.

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Note: Professional translator Alena Kašpárková, Prostějov, Czech Republic