

Study on the Possibilities to Use Ashes, EAF Dust and Lime Sludge as Neutralising Agent in Bioleaching

Chandra Sekhar Gahan¹, Maria Lucelinda Cunha² and Åke Sandström*,¹

¹Division of Process Metallurgy, Luleå University of Technology, SE-971 87 Luleå, Sweden and ²Dept. Ciência dos Materiais/CENIMAT, FCT/UNL, 2829-516 Caparica, Portugal

Abstract: Studies were conducted to investigate the possibilities to use combustion ashes, electric arc furnace (EAF) dust and lime sludge as neutralising agent with reference to a commercial grade slaked lime. To maintain optimum pH during biooxidation of pyrite the acid produced has to be neutralised. Batch bioleaching was performed on a pyrite concentrate in 1-L reactors, using a mixed mesophilic culture at a temperature of 35°C. Neutralising agents were added regularly to adjust pH to the desired level of 1.5. The ashes used were Bioash, Waste ash and Coal & Tyres ash, representing ashes generated from combustion of biomass, a mixture of wood chips and municipal waste, and a mixture of coal and tyres. The dust used was an EAF dust produced in a scrap-based steel plant, while the sludge used was Mesalime produced in a paper and pulp plant.

The study aimed to investigate the possibility to replace the conventionally used lime or limestone with by-products, based on their neutralising capacity and to observe eventual toxic effects on the bacterial activity. The bioleaching efficiency was similar for all the neutralising agents used except Waste ash, when compared with slaked lime. The extent of pyrite oxidation was in the range 69–75% for all neutralising agents, except Waste ash, which had a pyrite oxidation of 59%. The Waste ash contained a large number of potentially toxic elements and the chloride concentration of 11% probably had a negative effect as observed on the lower redox potential and pyrite oxidation. The EAF dust has a good potential to be used as neutralising agent in bioleaching processes for zinc recovery from zinc sulphides, due to the high content of zinc, however the chlorides present should be removed prior to its use.

The neutralising capacity, as determined by the amount needed for neutralisation during bioleaching, were rather high for EAF dust, Bioash and Mesalime with 37 g, 33 g and 29 g, respectively as compared with 22 g needed for slaked lime. However, Waste ash and Coal & Tyres ash had lower neutralising capacities with 81 g and 57 g needed, respectively. It is concluded that the replacement of lime or limestone with ash, dust or lime sludge can render considerable cost savings to the bioleaching operation. In addition, it is a means for sustainable use of natural resources, which would provide opportunities to recycle elements present in them like for example zinc.

Key Words: Bacteria, ash, dust, slime, pyrite, neutralisation, bioleaching.

1. INTRODUCTION

Biooxidation and bioleaching processes are mainly applied in heap and stirred tank leaching processes for the extraction of metal values from sulphidic ores and concentrates. Heap bioleaching is carried out on low-grade copper ores with 1–3% copper, mainly on secondary sulphide minerals as covelite (CuS) and chalcocite (Cu_2S), while tank leaching is done on refractory gold concentrates. In the bioleaching process, the microorganisms play a role in converting insoluble metal sulphides (zinc, copper, nickel, cobalt) or oxides (uranium) into water-soluble metal sulphates, whereas in the biooxidation process, which is applied on refractory gold concentrates, the role of the microorganisms are to decompose the mineral matrix, thereby exposing the entrapped gold for cyanide leaching. Dissolution of metal sulphides is controlled by two different reaction mechanisms i.e., the thiosulphate pathway and the polysulphide pathway.

The thiosulphate pathway is only applicable to the acid insoluble metal sulphides such as pyrite, molybdenite and tungstenite, while the polysulphide pathway is applicable for acid soluble metal sulphides like sphalerite, galena, arsenopyrite and chalcopyrite [1, 2].

The stirred tank biooxidation process has proved to be advantageous over heap bioleaching because the heap leaching process takes months and years to complete in comparison to only a few days needed in tank biooxidation process [3]. Stirred tank biooxidation of refractory gold concentrates and in one case on a cobaltic pyrite concentrate is currently used in more than ten full-scale operations using two different technologies with three more plants coming up in the near future [3–6]. New developments in stirred tank processes have come with high temperature mineral oxidation, which has been set up in collaboration between BHP Billiton and Codelco in Chile [3]. Most of the commercial application of stirred tank reactors uses Gold field's proprietary BIOX® process, while three are using the Canadian-based BacTech Mining Company's BACOX process for the treatment of refractory gold concentrates [3]. BHP Billiton Ltd operates pilot and demonstration scale processes for the re-

*Address correspondence to this author at the Division of Process Metallurgy, Luleå University of Technology, SE-971 87 Luleå, Sweden; Tel: +46 920 491290; Fax: +46 920 491199; E-mail: ake.sandstrom@ltu.se

covery of base metals from metal sulphides of nickel, copper and zinc by stirred tank bioleaching [7]. Bioleaching of zinc sulphides has been widely investigated at laboratory scale by various researchers [8-15]. The possibilities to process low-grade complex zinc sulphide ores through bioleaching have received much attention and has been tested in pilot scale [12, 16]. MIM Holdings Pty, Ltd. holds a patent for a fully integrated process that combines bioleaching of zinc sulphides with solvent extraction and electrowinning of zinc metal [17].

In the biooxidation of sulphide minerals, neutralisation of the acid produced is commonly practised with limestone. Neutralisation is required at three different stages in a bioleaching process for base metal recovery, as stated in Fig. (1). First, neutralisation is carried out at a pH ~1.5 during bioleaching with the help of limestone, the second neutralisation is done at pH 3-4 using lime or limestone to precipitate iron and arsenic, while the third neutralisation is done at pH 7-8 by lime to treat the final effluent (Fig. 1). Stirred tank biooxidation is carried out with finely ground high-grade mineral concentrates in highly aerated continuous flow reactors at temperatures ranging from 40-50°C. The mineral decomposition takes place in the pulp flowing through the series of stirred tanks with controlled pH, temperature and aeration. The pH in the reactors is maintained between 1.0-2.0 by addition of limestone, or if the concentrate contains acid consuming gangue minerals sulphuric acid is used to avoid jarosite precipitation at higher pH or foam formation at

lower pH [18, 19]. Control of pH at a desired level increases the process efficiency, while the use of a cheap neutralising agent increases the cost efficiency of the stirred tank biomining process. After biooxidation of the refractory gold concentrates, the bioleached residues is cyanide leached for gold recovery, while the ferric iron and arsenate in the leach liquor is precipitated in the form of ferric arsenate [20]. The precipitation of ferric arsenate is generally carried out with neutralising agents like lime/limestone. Studies conducted on the use of oxidic industrial by-products for precipitation of Fe/As from leaching solution by Cunha *et al.* shows that ashes, dust and mesalime are highly reactive due to the presence of calcite and lime [21]. Due to the extensive use of neutralising agents in various steps of biomining and the relatively high cost associated with it, researchers and industries have tried to find substitutes to lime/limestone. Important criteria for choosing an alternative neutralising agent are; the neutralising capacity; no toxic effects for the micro-organisms; the distance between the bioleaching plant and the source of neutralising agent should be short; and finally, the cost of the neutralising agent should be cheaper than the generally used lime/limestone.

Sweden produces a large quantity of non-coal ashes every year. In 2003, the estimated total amount of ash produced was 1,125,000 tons per annum, of which 715,000 tons was bottom ash and 410,000 tons fly ash. The fly ash and bottom ash produced in Sweden have different characteristics depending on their fuel source and type of boilers used.

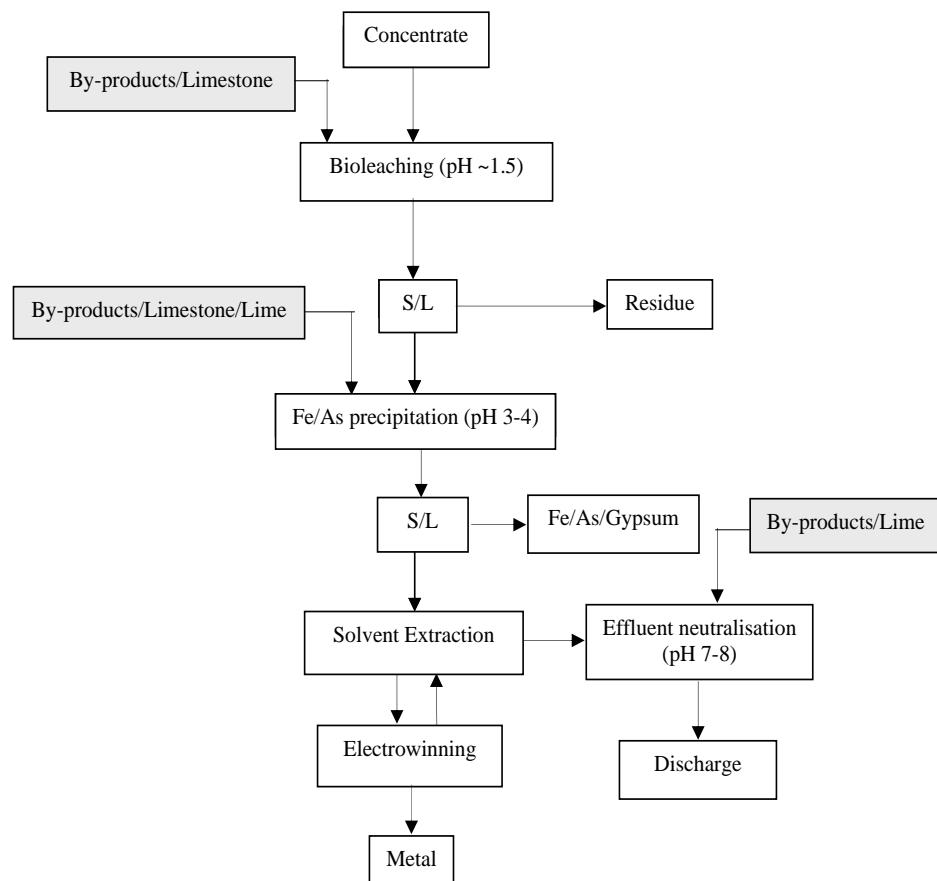


Fig. (1). Flow sheet of a process for base metal production describing stages of neutralisation.

The amount of ashes produced from different sources were 15–25% from municipal waste, ~5% from peat, 10–50% from sludge of paper industry, 2–4% from bark, 0.3–0.5% from pure wood [22]. All the non-coal ashes in Sweden have a high pH due to their high lime content. Use of ashes as a liner construction material in landfill is an option for the utilisation of the ashes, but in Sweden, many landfills are going to be closed in the next 10–15 years [22, 23]. Therefore, alternative applications should be looked for to use ashes in various other aspects. Studies conducted on use of three types of coal combustion ashes generated from a power plant in Illinois, USA suggested that they could be used as a neutralising agent in agriculture, waste treatment, fertilisers, wallboards, concrete and cement production, ceramics, zeolites, road construction and manufacture of amber glass [24]. Acid mine drainage mitigation can be another alternative use of fly ash. Studies conducted by Hallberg *et al.* stated that the acid mine drainage generated in Falun, Sweden could be prevented by covering the sulphide mine tailings with a mixture of fly ash and biosludge [25].

Electric arc furnace (EAF) dust recovered from the gas cleaning system of scrap based steel production is an industrial oxidic by-product with high content of zinc. It is only about 1.5% of the total output from a typical steel industry, but can create major environmental problems, which needs to be handled carefully. The material comprises of zinc, calcium, iron, and silicate with contaminants of heavy metals such as lead, cadmium, chromium and others. Since 1984, due to the presence of small quantities of heavy metals, mainly lead in the EAF dust, it has been regulated as a hazardous waste under the U.S. EPA's solid waste Resource Conservation and Recovery Act (RCRA) [26]. Steel industries have installed elaborate dust collection systems to control the dust due to its hazardous nature. Every steel industry and electric arc furnace user pays millions of dollars for removal, treatment and disposal of the EAF dust. Part of the EAF dust produced is sent to industries for recycling, while parts are shipped to hazardous waste landfills, where it is chemically treated, and buried at a cost of more than US dollars 100 per ton. In addition to posing a tremendous potential liability to the steel industries, the landfilled dust also contains significant and valuable quantities of recoverable zinc. Studies on hydrometallurgical processing for recovery of zinc from EAF dust have been widely carried out by various researchers [27–30]. In a future plant for bioleaching of zinc sulphide EAF dust can be a potential neutralising agent as it would then enrich the zinc concentration in the leachate [21].

Lime sludge, a by-product generated from paper and pulp industry is reused for production of lime (calcium oxide) by calcination, at temperature ranging from 1000° C to 1300° C, and marketed as quicklime and hydrated lime [31]. Some part of the lime sludge has to be bled out, due to formation of metakaolin on calcination [32]. Therefore, alternative use of lime sludge generated from the paper industry can save the cost incurred for the landfill.

The use of oxidic by-products as neutralising agent is expected to be useful due to its high alkalinity, availability and cost effectiveness in comparison to limestone. A comparative cost analysis conducted on limestone with different neutralising agents [33] states that the cost of limestone was one-third to that of slaked lime. As industrial oxidic by-

products are much cheaper than limestone, their use as a neutralizing agent would benefit to the cost efficiency of the process. The aim of the present investigation is to study the possibilities to use ashes, dust and lime sludge generated from different Swedish industries as neutralising agents in a bioleaching operation. Batch bioleaching experiments on a highly acid producing pyrite concentrate were conducted to determine the neutralising capacity of the ashes, dust and lime sludge, and observe any eventual toxic effects on the microorganisms used.

2. MATERIALS AND METHOD

2.1. Microorganisms

The microbial cultures for all bioleaching experiments were taken from a continuous reactor in order to have an identical bacterial culture for the start up of the experiments. The culture was growing on the 9K nutrient medium [34] supplemented with 4.5 g/L of Fe²⁺ and 2 mM of potassium tetrathionate at a dilution rate of 0.021 h⁻¹. The continuous reactor was maintained at a pH level of 1.45 ± 0.05 and a redox potential of 740 ± 5 mV vs. Ag/AgCl. The mixed culture used in the experiments contained iron oxidisers, sulphur oxidisers and a few archaeal species, as determined through Q-PCR analysis by Bioclear B.V., Netherlands. Dominating species in the culture were *Leptospirillum ferrooxidans*, *Acidithiobacillus caldus*, *Acidithiobacillus thiooxidans*, *Sulphobacillus* sp. and *Ferroplasma* sp.

2.2. Analytical and Instrumentation Techniques

Total iron concentrations in the leach liquor samples were analysed by Atomic Absorption Spectroscopy (AAS). Redox potential was measured with a platinum electrode against the Ag, AgCl reference electrode, and a Lange LDO™/sc100 was used for the measurement of dissolved oxygen. Elemental analysis of the pyrite concentrate, neutralising agents and bioleaching residues were accomplished by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)/Quadrupole Mass Spectrometry (ICP-QMS)/Sector Field Mass Spectrometry (ICP-SFMS). X-ray powder diffraction (XRD) on by-products and leaching residues was performed using a Siemens D5000 automatic diffractometer equipped with a continuous scanning device. Cu Kα radiation of 40 kV and 30 mA and a sample rotation of 30 rpm were used. Diffraction patterns were measured in the range from 10° to 90° and crystalline phases were identified using the Joint Committee for Powder Diffraction Standards (JCPDS) file of the instrument.

2.3. Pyrite Concentrate

The pyrite concentrate used for bioleaching was obtained from the tailings of a chalcopyrite flotation at the Boliden plant in Aitik, Sweden. Elemental composition of the concentrate showed the presence of sulphur, 23.9% and iron, 25.7% as major constituents, and relatively high amounts of silicon and aluminium, 12.9% and 4.5%, respectively (Table 1). Mineralogical phases identified in the concentrate were pyrite (FeS₂), which was dominating, and kyanite (Al₂SiO₅), a gangue mineral.

2.4. Neutralising Agents

Industrial oxidic by-products, like ashes, dust and lime sludge, generated from different Swedish industries was used

as neutralising agents in the bioleaching experiments. Three different types of ashes from combustion for power generation were used. Bioash is a mixture of fly and bottom ash generated during combustion of biomass. Coal & Tyres ash is a fly ash from combustion of a mixture with 67% coal and 33% tyres. Waste ash is a mixed fly ash from combustion of wood chips and municipal waste. The EAF dust used is a dust collected in the gas cleaning system of an electric arc furnace in scrap based steel production. The lime sludge used was Mesalime generated in a paper and pulp industry. A chemical grade slaked lime, $\text{Ca}(\text{OH})_2$, was used as the reference material.

The Mesalime was dried at 65°C for 22 h to remove its water content. All by-products were ring milled for 20 seconds before used except slaked lime, which was used as received. Particle size analysis by laser size classification was carried out on all samples. Final grind size of the particles expressed as 80% passing (d_{80}) was in the range of 15–25 μm for the by-products. The particle size for the calcium

hydroxide reference material was the finest with a d_{80} of 8 μm [35]. The by-products used for the study were characterised chemically and mineralogically (Tables 2 and 3) [35]. All the neutralising agents were added directly into the pulp in the form of powder.

2.5. Bioleaching

Batch experiments were performed for bioleaching of the pyrite concentrate in a glass reactor with a working volume of 1 L. An airtight lid with a condenser was used to minimize evaporation from the reactor. A hot plate heater was placed below the reactor to maintain the temperature at 35°C in the reactor. A propeller stirrer was fixed at a height of 1.5 cm above the base of the reactor at a rotation speed of 250 rpm for homogenous mixing of the pulp. Two baffles were mounted perpendicular to the vessel wall to avoid vortex formation. Air enriched with CO_2 (2-3%, v/v) was blown into the bioreactor at a rate of 1 L/min beneath the propeller resulting in a dissolved oxygen (D.O.) level of 5 mg/L in the

Table 1. Elemental Composition of the Pyrite Concentrate

Material	Composition (%)														
Pyrite concentrate	Si	Al	Ca	Fe	K	Mg	Mn	Na	S	Ba	Cu	Cr	Mo	Zn	
	12.9	4.5	1.9	25.7	2.3	0.7	0.2	0.7	23.9	0.6	0.2	0.01	0.01	0.01	

Table 2. Elemental Composition of the Neutralising Agents

Neutralising Agents	Si (%)	Al (%)	Ca (%)	Fe (%)	K (%)	Mg (%)	Mn (%)	Na (%)	S (%)	Ba (mg/kg)	Cr (mg/kg)	Mo (mg/kg)	Pb (mg/kg)	V (mg/kg)	Zn (mg/kg)	F (mg/kg)	Cl (mg/kg)
$\text{Ca}(\text{OH})_2$	0.1	0.0	53.6	0.0	0.1	0.4	0.0	<0.004	0.02	<2	<10.0	<6.0	1.9	<2.0	27.3	30.9	1047
Bioash	1.5	0.3	30.7	0.6	6.9	3.3	3.7	0.1	0.53	5630	65.1	<6	30.8	5.5	1420	138	1900
Waste ash	8.0	4.0	12.3	4.6	4.5	1.5	0.2	4.6	5.22	1840	584	47.3	7670	57.9	83900	3624	110050
Coal & Tyres ash	3.2	1.4	23.0	1.5	0.4	0.5	0.0	0.3	6.87	463	39.8	<6	154	60.4	44000	362	9531
EAF dust	1.2	0.4	13.9	20.1	0.8	0.9	2.9	0.7	0.43	308	1300	49.5	7280	21.9	241000	846	15225
Mesalime	0.1	0.1	38.2	0.1	<0.1	1	0.1	0.7	0.03	145	23.8	<6	2.30	10	96.7	41.6	1144

Table 3. Mineralogical Phases of Neutralising Agents Identified by XRD

Neutralising Agents	Phases Identified by XRD
$\text{Ca}(\text{OH})_2$	portlandite ($\text{Ca}(\text{OH})_2$)
Bioash	calcite (CaCO_3), calcium manganese oxide ($\text{Ca}_3\text{Mn}_2\text{O}_7$), carbon (C), lime (CaO), periclase (MgO)
Waste ash	halite (NaCl), quartz (SiO_2), calcium sulphate (CaSO_4), periclase (MgO), potassium magnesium silicate (K_2MgSiO_4), calcium aluminium oxide (CaAl_2O_4)
Coal & Tyres ash	calcium sulfate sulfite ($\text{Ca}_3(\text{SO}_3)_{2.12}(\text{SO}_4)_{0.88}$), calcium sulfite hydrate ($\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$), carbon (C), portlandite ($\text{Ca}(\text{OH})_2$), zincite (ZnO)
EAF dust	franklinite (ZnFe_2O_4), lime (CaO), zincite (ZnO), calcium manganese oxide ($\text{Ca}_3\text{Mn}_2\text{O}_7$), manganese zinc iron solid solution ($\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_{1-y}\text{Fe}_2\text{O}_3$)
Mesalime	calcite (CaCO_3)

bioleaching pulp. The experiments were performed with 10% (w/v) of concentrate and 10% (v/v) inoculum with the iron free 9K mineral salt medium [34].

Due to the presence of acid consuming gangue in the concentrate, pH was adjusted to 1.5 with H₂SO₄ during the initial days of the experiments. The bacterial activity was followed by measurements of pH and redox potential once or twice daily. The pH was adjusted to 1.5 by additions of ashes/dust/lime sludge (or slaked lime) whenever required. The bioleaching experiments continued until no further changes in pH and redox potential were observed. Leach

liquor was drawn every second day from the bioreactor during the course of bioleaching and analysed by AAS for the total iron concentration to follow the bioleaching trend. After completion of each experiment, the pulp was harvested by filtration and the filter cake was washed with a measured volume of deionised water, acidified to pH 1.5 with H₂SO₄. Total volume of leach liquor including wash water, was measured before analysis (Table 6). The washed bioleach residues were dried in a hot air oven at 70 °C for several days. Bioleach residues were analysed chemically and mineralogically (Tables 4 and 7).

Table 4. Elemental Composition of the Bioleach Residues

Bioleach Residues	Si (%)	Al (%)	Ca (%)	Fe (%)	K (%)	Mg (%)	Mn (%)	Na (%)	S (%)	Ba (mg/kg)	Cu (mg/kg)	Cr (mg/kg)	Mo (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Ca(OH) ₂	10.8	2.9	10.9	11.9	1.9	0.2	0.1	0.7	11.4	4840	645	29.0	104	32.5	43.0
Bioash	9.3	2.4	8.2	15.2	3.2	0.1	0.1	0.7	12.2	5480	485	52.6	93	39.5	<20
Waste ash	10.8	2.8	6.4	15.7	3.2	0.4	0.1	0.9	11.8	4230	839	271	98	6820	6600
Coal & Tyres ash	10.3	2.9	10.0	10.6	1.7	0.2	0.1	0.7	11.6	4300	500	34.1	82.7	83.9	1130
EAF dust	11.2	3.1	5.5	18.1	2.2	0.3	0.5	0.8	10.7	5090	956	1020	117	2390	18800
Mesalime	11.5	3.1	10.4	11.7	2.1	0.2	0.1	0.8	11.9	5400	607	24.4	108	33.7	29.7

Table 5. Elemental Composition of the Bioleach Liquors

Neutralising Agents	Composition												
	Fe (g/L)	Al (g/L)	SO ₄ ²⁻ (g/L)	Ca (mg/L)	Si (mg/L)	K (mg/L)	Mg (mg/L)	Mn (mg/L)	Na (mg/L)	Cu (mg/L)	Zn (mg/L)	F (mg/L)	Cl (mg/L)
Ca(OH) ₂	8.7	0.8	27.6	536	197	<10	426	43.6	21.2	93.6	14.3	N.A.	N.A.
Bioash	3.1	0.9	25.6	495	336	<5	1190	976	39.9	85.8	63.4	N.A.	N.A.
Waste ash	1.0	3.3	29.7	505	416	486	1160	117	3190	344	5720	313	8910
Coal & Tyres ash	8.9	0.9	34.2	550	395	<5	518	45.7	62.2	93.4	1790	33	464
EAF dust	9.8	0.9	42.9	513	237	<5	512	569	118	132	5820	48	519
Mesalime	9.6	0.9	33.9	520	358	<5	607	79	131	102	15.3	N.A.	N.A.

*N.A. : Not analysed

Table 6. Experimental Results

	Ca(OH) ₂	Bioash	Waste Ash	Coal & Tyres Ash	EAF Dust	Mesalime
Neutralising agent addition, (g)	22.1	32.7	81.5	57.0	37.5	28.7
Concentrate addition, (g)	100.0	100.0	100.0	100.0	100.0	100.0
Bioleach residue, (g)	127.8	147.4	180.0	151.1	123.3	121.0
Wash water, (L)	0.25	0.35	0.35	0.35	0.25	0.22
Bioleach filtrate, (L)	1.19	1.23	0.90	1.24	1.15	1.14
Pyrite oxidation, (%)	74.9	68.7	59.1	75.3	69.8	72.6

2.6. Calculation of Pyrite Oxidation

During bioleaching of pyrite, part of the ferric iron in solution precipitated as ferric hydroxide, jarosite and possibly other basic ferric sulphates. In order to obtain the total extent of pyrite oxidation, the precipitates in the residues were dissolved in 6 M HCl. This treatment does not dissolve pyrite. The residues might also contain un-dissolved iron originating from the ashes/dust/lime sludge, which has to be accounted for in the oxidation calculation. Therefore, the amount of soluble iron in 6 M HCl in the ashes/dust/lime sludge was determined, and the recovery based on feed and residue analysis was thus calculated according to the following formula:

$$\text{Oxidation} = \left(1 - \frac{\text{Fe(r)} - \text{Fe(sr)} - \text{Fe(nss)}}{\text{Fe(f)}} \right) \times 100, \text{ where Fe(r)}$$

is the iron content in residue, Fe(sr) is the soluble iron content in residue, Fe(nss) is the content of non soluble iron in the ashes/dust/lime sludge and Fe(f) is the iron content in the pyrite.

3. RESULTS

3.1. Bioleaching with Ca(OH)₂ as a Reference Neutralising Agent

During the initial stage of this experiment, enough care was not taken to avoid fluctuations in pH, which disturbed the bacterial growth resulting in a lag phase that lasted 12 days, which can be observed from the slow trend of increase in redox potential (Figs. 2 and 3). When a good bacterial activity was obtained after the initial disturbances, the pH in the experiment varied between 1.25-1.59 (Fig. 2). The highest bioleaching activity was between day 18 and 23 during which time most of the slaked lime was added. During night, when no additions were made, pH decreased considerably as seen in Fig. (2). The total amount of calcium hydroxide needed for neutralisation during bioleaching of the pyrite concentrate was 22.1 g (Table 6). The dry solid residue obtained after bioleaching weighed 128 g, i.e. more than the total amount of solids introduced into the reactor, due to the formation of gypsum. Other phases identified in the residue

Table 7. Mineralogical Phases of Bioleach Residues Identified by XRD

Bioleach Residues	Phases Identified by XRD
Ca(OH) ₂	gypsum (CaSO ₄ .2H ₂ O), jarosite hydronian ((K,H ₃ O)Fe ₃ (SO ₄) ₂ (OH) ₆), microcline intermediate (KAlSi ₃ O ₈), pyrite (FeS ₂)
Bioash	gypsum (CaSO ₄ .2H ₂ O), jarosite hydronian ((K,H ₃ O)Fe ₃ (SO ₄) ₂ (OH) ₆), quartz (SiO ₂)
Waste ash	gypsum (CaSO ₄ .2H ₂ O), jarosite (KFe ₃ (SO ₄) ₂ (OH) ₆), pyrite (FeS ₂), quartz (SiO ₂)
Coal & Tyres ash	gypsum (CaSO ₄ .2H ₂ O), jarosite hydronian ((K,H ₃ O)Fe ₃ (SO ₄) ₂ (OH) ₆), pyrite (FeS ₂), quartz (SiO ₂)
EAF Dust	gypsum (CaSO ₄ .2H ₂ O), jarosite (KFe ₃ (SO ₄) ₂ (OH) ₆), franklinite (ZnFe ₂ O ₄ / Fe ₂ O ₃ .2SO ₃ .H ₂ O), quartz (SiO ₂)
Mesalime	gypsum (CaSO ₄ .2H ₂ O), jarosite (KFe ₃ (SO ₄) ₂ (OH) ₆), quartz (SiO ₂)

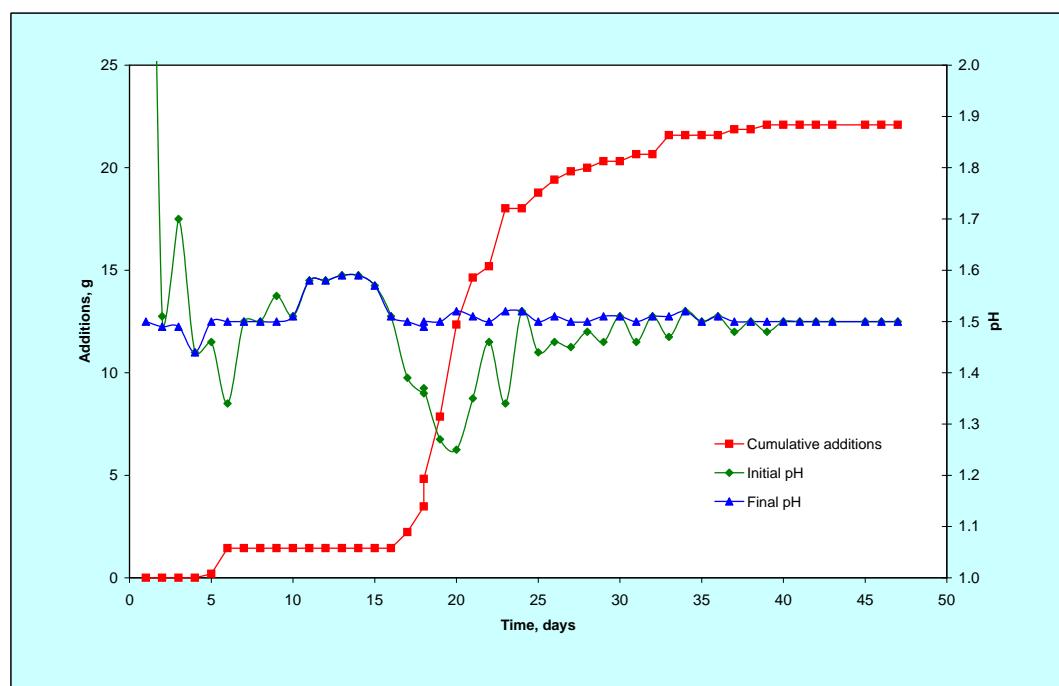


Fig. (2). Change in redox potential and iron concentration with addition of Ca(OH)₂.

by XRD include hydronian jarosite, minor amounts of unleached pyrite and the silicate microcline (Table 7).

The total iron and sulphate content in the leach solution was 8.7 g/L and 27.6 g/L, respectively (Fig. 5, Table 5). Apart from iron, also some aluminium (0.8 g/L) and magnesium (0.4 mg/L) dissolved from the pyrite concentrate (Table 5). The sulphate concentration in the leachate was 27.6 g/L and in this reference experiment 75% of the pyrite was oxidised (Table 6).

3.2. Bioleaching with Bioash as Neutralising Agent

The lag phase was relatively short in this experiment with an increase in redox potential after 6 days (Fig. 4). The reactivity of the Bioash was relatively high, which made it easy to control the pH at the desired level after the acid consuming gangue had been neutralised, the pH in the experiment varied between 1.18 and 1.54. The highest activity with respect to acid production was between day 15 and 18 when the bulk of the neutralising agent was needed (Figs. 4 and 6).

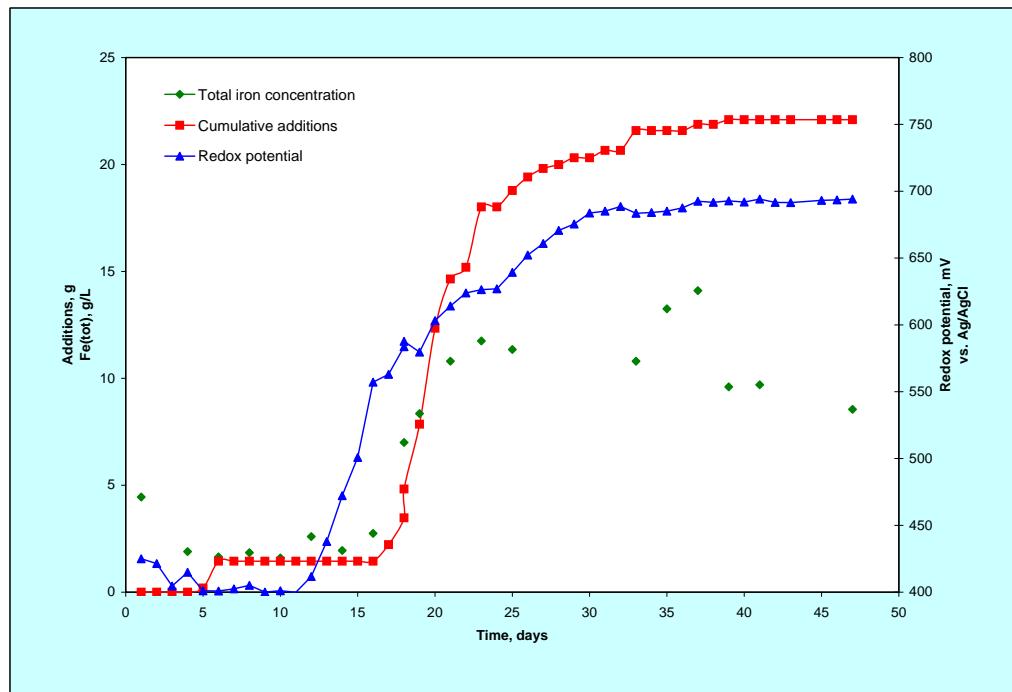


Fig. (3). pH before and after addition of $\text{Ca}(\text{OH})_2$.

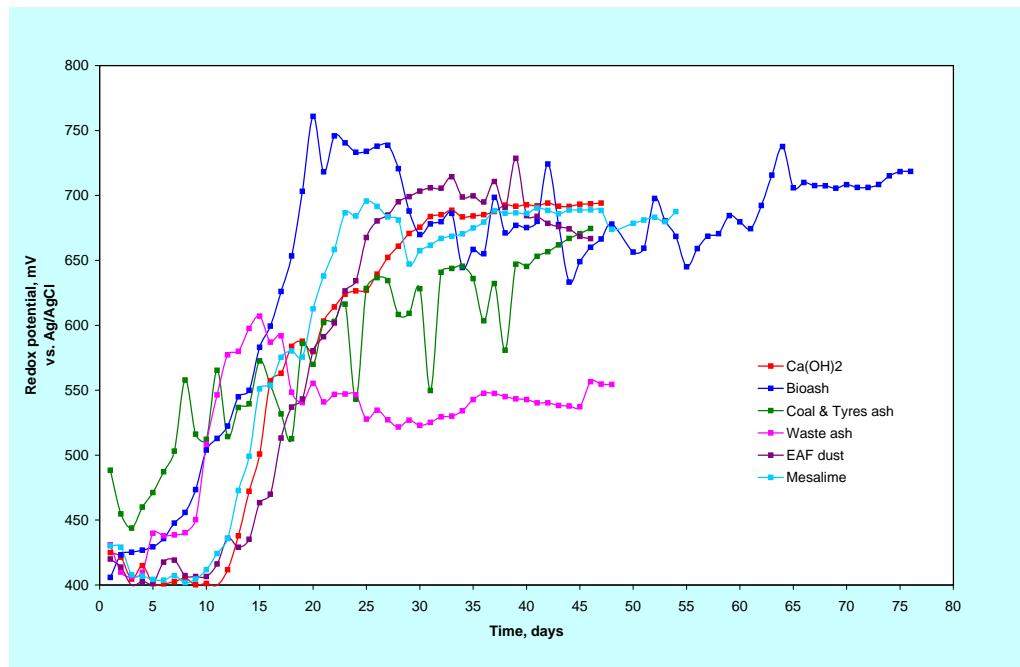


Fig. (4). A plot of redox potential vs. time in the experiments with reference to slaked lime.

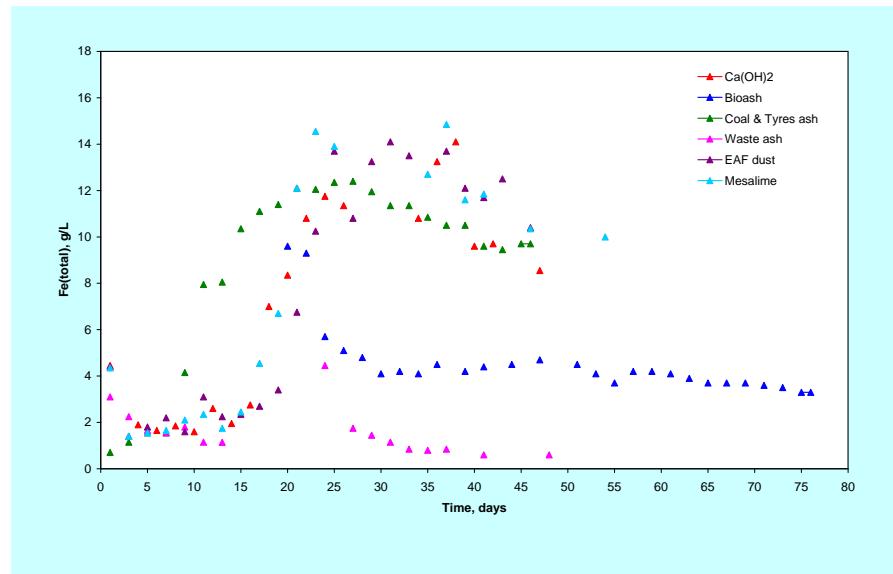


Fig. (5). A plot of total iron concentration vs. time in the experiments with reference to slaked lime.

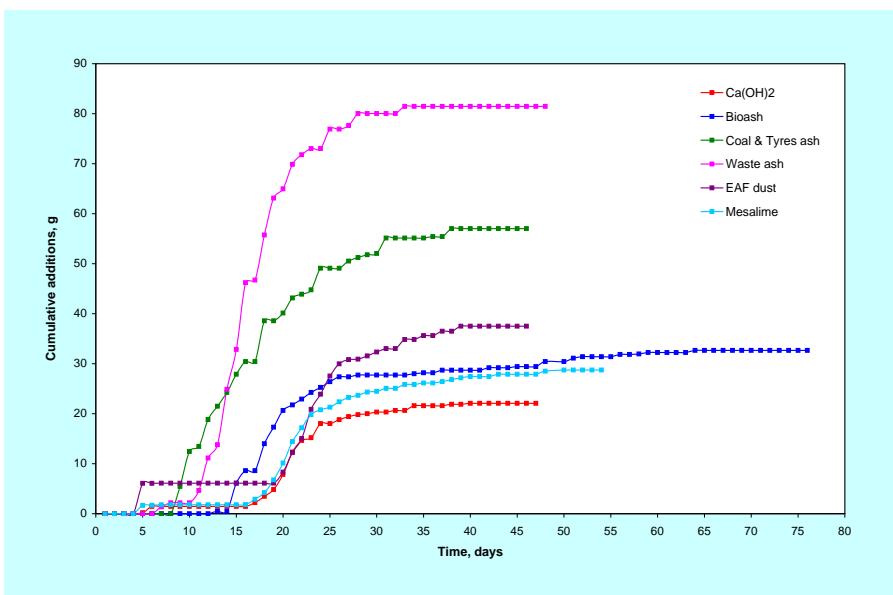


Fig. (6). A plot of additions vs. time in the experiments with reference to slaked lime.

The redox potential reached a maximum of about 750 mV after 20 days and thereafter it had a decreasing trend with relatively big daily fluctuations giving a final value around 710 mV (Fig. 4). The total amount of Bioash added was 32.7 g and the dry residue weight was 147.4 g (Fig. 6, Table 6). Crystalline mineral phases identified by XRD were gypsum, hydronian jarosite and free quartz (Table 7).

The final leach liquor contained 3.1 g/L of iron, but as can be seen in Fig. (5), the concentration decreased gradually from almost 10 g/L after 20 days. The solution had a sulphate concentration of 25.6 g/L together with concentrations of approximately 1 g/L of aluminium, magnesium and manganese (Table 5). The content of magnesium and manganese in the Bioash was 3.3% and 3.7%, respectively (Table 2), which gives leaching yields of these elements of about 85%. The pyrite oxidation was found to be 68.7% (Table 6).

3.3. Bioleaching with Waste Ash as Neutralising Agent

The pH was relatively easy to control with Waste ash, since it did not contain minerals with slow dissolution rates, and after the initial days, pH varied in the range 1.30-1.56 (Fig. 6). After an initial increase in redox potential up to 607 mV on day 15 and with acid production, the redox potential, suddenly within 3 days, decreased below 550 mV and remained at that level until the experiment was stopped (Fig. 4). However, smaller amounts of acid continued to be produced until day 30, which was neutralised by more additions of ash (Fig. 6). The total amount of Waste ash added was 81.5 g, which was the biggest amount needed in all experiments and the amount of dry residue obtained after filtration was 180 g (Fig. 6, Table 6). The XRD diffractogram of the residue revealed in addition to gypsum, mineralogical phases of jarosite, pyrite and free quartz (Table 7).

The iron concentration in the leachate was low throughout the entire experiment and was only 1 g/L at the end of the experiment (Fig. 5, Table 5). The sulphate, aluminium and magnesium concentrations in the final leachate obtained were 29.7 g/L, 3.3 g/L and 1.2 g/L, respectively (Table 5). Chloride was present in the ash as highly soluble halite (Table 3) giving a chloride concentration of 8.9 g/L in the leachate (Table 5). The content of zinc in Waste ash was 8.4% (Table 2) of which 75% dissolved, giving a zinc concentration of 5.7 g/L (Table 5). Vacuum filtration of the pulp was difficult and took much longer time than in the other experiments and therefore the volume of final leachate was only 900 ml. The pyrite oxidation was 59%, which was the lowest among all the experiments (Table 6).

3.4. Bioleaching with Coal & Tyres Ash as Neutralising Agent

The pH varied in the range 1.32-1.57 throughout and was relatively easy to control (Fig. 6). The redox potential increased steadily but slowly during the course of the experiment. Notable is (Figs. 4 and 6) that after each ash addition, the redox potential decreased, in some cases with as much as 15 mV. The amount of Coal & Tyres ash consumed in the experiment was 57 g, and the dry residue weighed 151 g (Fig. 6, Table 6).

The final bioleach liquor had a concentration of 8.9 g/L iron and 34.2 g/L sulphate ions (Fig. 5, Table 5). The ash contained 4.4% zinc of which 89% dissolved resulting in a concentration of 1.8 g/L in solution (Table 2 and 5). Aluminium and magnesium concentrations of 0.9 g/L and 0.5 g/L respectively were similar to that obtained in the experiment with slaked lime (Table 5). Mineralogical phases of gypsum, hydronian jarosite, pyrite and free quartz were identified by XRD analysis of the bioleached residue (Table 7). The experiment with Coal & Tyres ash resulted in a pyrite oxidation of 75.3%, which was slightly higher than the reference experiment with Ca(OH)₂ (Table 6).

3.5. Bioleaching with EAF Dust as Neutralising Agent

Initially when the bacteria became active, too much dust was added leading to a too high pH, which had to be lowered by additions of acid. The slightly too high pH remained until day 17 when bacterial acidity production lowered it to 1.5 again (Fig. 6). This disturbance made the lag phase longer but did not affect the bacteria negatively as is seen by a steady increase in redox potential from day 14 and onwards (Fig. 4). During the last 14 days, the redox potential gradually decreased to 660 mV from values above 700 mV (Fig. 4). The total amount of EAF dust used for neutralisation was 38 g and the dry residue weighed 123 g (Fig. 6, Table 6).

In the bioleachate, the analysed iron and sulphate concentrations were 9.8 g/L and 42.9 g/L, respectively, while the aluminium and magnesium concentrations were 0.9 g/L and 0.5 g/L, respectively (Fig. 5, Table 5). The EAF dust had a high content of zinc (24.1%) (Table 2), which dissolved to an extent of 74% during leaching, giving a concentration of 5.8 g/L in solution (Table 5). The chloride concentration in the leachate was 0.5 g/L due to the presence of highly soluble chlorides in the dust. Crystalline phases of franklinite, jarosite and iron sulphate hydroxide together with gypsum and free quartz were identified by XRD in the residue (Table

7). In this experiment, a pyrite oxidation of 70% was achieved (Table 6).

3.6. Bioleaching with Mesalime as Neutralising Agent

Also in this experiment slightly too much material was added in the beginning resulting in a high pH initially (Fig. 6). A steady increase in the redox potential was seen from day 11 and during the last 20 days of the experiment the redox potential remained at around 680 mV (Fig. 4). The amount of Mesalime needed for neutralisation was 29 g and the weight of the residue was 121 g, which was the lowest weight obtained in all experiments (Fig. 6, Table 6).

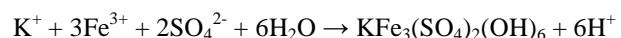
Concentrations of 9.6 g/L of iron and 34 g/L of sulphate were found in the leaching solution (Fig. 5, Table 5). The lime sludge was a relatively pure product containing mainly calcite (Tables 2 and 3) and therefore the metal concentrations obtained in the leachate are very similar to what was obtained with slaked lime (Table 5). Apart from gypsum, phases of jarosite and free quartz were identified in the residue (Table 7). The pyrite oxidation was 72.6%, which also was similar to the reference experiment (Table 6).

4. DISCUSSION

The purpose with the present study is to investigate if by-products like ashes, sludge and dust can be used as neutralising agent in bioleaching operations. Important to consider, apart from their neutralising capacity, is also if the by-product to be used contains elements that might be toxic for the microorganisms. To conduct the study a pyrite concentrate was chosen since pyrite generates high amounts of acid when it is oxidised. Comparison of the pyrite oxidation in the different experiments shows that the experiment with Coal & Tyres ash and slaked lime both resulted in 75% pyrite oxidation. The experiments with EAF dust, Bioash and Mesalime all had pyrite oxidation in the range from 69% to 73%, while in the experiment with Waste ash the pyrite oxidation was only 59% (Table 6). Regarding neutralisation capacity, i.e. the amount of oxidic by-products needed to maintain pH at the required level, all by-products needed higher amounts than slaked lime. Mesalime required 30% more than slaked lime, which reflects the difference in molecular weight between Ca(OH)₂ and CaCO₃. The EAF dust and Bioash had relatively high neutralising capacities and needed 70% and 48% more additions, respectively, to achieve the same neutralisation as slaked lime. The Waste ash and Coal & Tyres ash had lower neutralising capacities and required an amount of 2.6 and 3.7 times the amount needed for the experiment with slaked lime (Table 6).

The total iron concentration increased during the first 3-4 weeks of bioleaching, thereafter, the iron concentration started to decrease due to the precipitation of ferric iron as jarosite and possibly other basic sulphates (Fig. 5, Table 7). The kinetics for jarosite precipitation at 35°C is known to be relatively slow, but the long duration of batch bioleaching experiments enhanced the jarosite precipitation, which was confirmed by XRD analysis of the bioleaching residues (Table 7) [9]. Potassium jarosite is among the least soluble jarosites and it was seen in the experiments with Bioash and Waste ash, which both had high potassium content, 6.9% and 4.5%, respectively (Table 2), that jarosite precipitated to a great extent. In the experiments with these ashes, the ferric

iron concentrations were much lower than what was obtained with the other materials (Fig. 5, Table 5). In the case of Waste ash the total iron concentration in the final leachate was only 1.0 g/L (Table 5) and with such low concentration, the pyrite leaching might also be affected since the oxidation proceeds through ferric iron. Jarosite precipitation lowers the redox potential due to the removal of ferric ions from the solution, and thereby leads to a lowering of the pH in the solution, according to the following formula:



This is probably what is seen in the later parts of most of the experiments, with gradual decrease in both the total iron concentration and the redox potential. The calcium content in the leachate obtained in all experiments was 0.5–0.6 g/L reflecting the limited solubility of calcium in sulphate medium (Table 5). The sulphate concentrations varied from 26 g/L for Bioash to 43 g/L for the EAF dust, while a concentration of 28 g/L was obtained in the experiment with Ca(OH)₂ (Table 5). The great variation in sulphate concentrations in the solution was due to the presence of various soluble metal sulphates of elements like zinc, magnesium and aluminium, apart from the iron sulphates.

The Waste ash was chosen as a worst case, since ashes from combustion of municipal waste are known to contain many different metal oxides, some of them potentially toxic like lead, cadmium and mercury. In addition, the Waste ash studied also contained high amounts of chlorine (11%) mainly as highly soluble halite (NaCl) as identified by XRD; fluorine, which is potentially toxic for the microorganisms [36], was also present in relatively high amounts (~0.4%). In a study [37], it was shown that biooxidation cultures were able to adapt to chloride levels up to 4.2 g/L, while greater concentrations gave inhibitory effects. When the experiment with Waste ash was examined, it was observed that the experiment started normally with an increase in redox potential that reached above 600 mV after 15 days (Fig. 4). However, after that the redox potential decreased to about 550 mV and remained at that level throughout the experiment. The total amount of ash added on day 16, when the redox potential started to decrease was 46 g, which then would give a chloride concentration of 5.1 g/L with the assumption that all chloride dissolved, i.e. the toxic level of chloride was probable exceeded during that time period. Also the Coal & Tyres ash and the EAF dust had elevated levels of chlorine, 1% and 1.6%, respectively (Table 2), but the concentrations obtained in the leachate when these materials were used was only 0.5 g/L (Table 5), which did not hamper the bacterial activity, since high redox potentials of 660–670 mV was obtained in these experiments (Fig. 4). Since chlorine in these materials is present as NaCl and possibly KCl, which both are very soluble in water, one possible pre-treatment to remove the chlorides would be to do a water leaching prior to their use as neutralising agents, which also has been practised to upgrade the zinc content in the EAF dust [28].

The Bioash and Coal & Tyres ash contained un-burnt carbon as identified by XRD and in the case of Coal & Tyres ash the colour was blackish and once added into the pulp it became oily and sticky to the reactor walls. It is also obvious from the behaviour of the redox potential (Fig. 4) that the ash contained something with reducing properties since upon

each addition the redox potential immediately decreased. The reason for this is not clear but it is believed that some organic component in the ash might be responsible for this behaviour. However, despite the disturbances in this experiment, it appeared to have high bacterial activity since the redox potential always recovered and increased throughout the experiment and resulted in a higher pyrite oxidation than the experiment with Ca(OH)₂ (Table 6).

Some of the by-products chosen had high zinc contents, which would add to the zinc tenor in the leachate. Use of these materials as neutralising agents in bioleaching would be a benefit especially in the case of a bioleaching process for zinc recovery. The concentration of zinc in the leachate obtained from the experiments with EAF dust, Waste ash and Coal & Tyres ash were 5.8 g/L, 5.7 g/L and 1.8 g/L, respectively (Table 5). The zinc oxide present in them dissolved readily, whereas ferrites like franklinite (ZnFe₂O₄) (Table 3) require higher temperatures and lower pH to dissolve. Franklinite was identified by XRD in the EAF dust and was also observed in the residue after leaching and due to its presence the zinc leaching yield in this experiment was 74% (Table 5). The Mesalime used in this study was the purest by-product investigated and consisted essentially of pure calcite (CaCO₃) giving similar results as the reference experiment with slaked lime.

5. CONCLUSIONS

The comparative study of by-products has proved that all materials investigated would be good substitutes for limestone for pH control in bioleaching operations, and in most cases without negative impact on the bioleaching efficiency. The Mesalime is the best alternative since it is practically a pure calcite, which is normally used. If the chlorides in the EAF dust were removed by a water-washing step preceding its use as neutralising agent this dust would be an excellent substitute for limestone, especially in a process for zinc recovery due to its high content of soluble zinc. Bioash is also a good alternative neutralising agent with high neutralising capacity due to its content of calcite and lime and relatively low content of other impurities. The Coal & Tyres ash is less suitable despite the presence of relatively high amounts of zinc since the organic compounds present in it would create material handling problems in the bioleaching process due to its sticky nature. The Waste ash was found to be the least suitable by-product due to the presence of high amounts of potentially toxic elements, low neutralising capacity and a low pyrite oxidation. The alternative use of the by-products would save the cost of landfill and at the same time reduce the operational cost for neutralisation thus making the bioleaching operation more economical. The only cost involved in the use of by-products is the transportation cost that depends on the distance between the industry producing oxidic by-products and the bioleaching plant, which might be less than the landfill cost. The use of oxidic by-products will render an environmentally friendly process and prevent over use of natural limestone deposits.

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