PRESSURE LEACHING OF SMELTER FLUE DUST: AN EXPERIMENTAL INVESTIGATION

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ABSTRACT. The investigation reported in this paper has been the initial phase of an experimental program to study the application of hydrometallurgical techniques to the recovery of copper and zinc from copper smelter flue dust. Flue dust is generated as a by-product of copper smelting operations and contains metals such as copper, zinc, iron, arsenic, cadmium, and lead. Characterization of the flue dust has been performed by means of chemical and X-ray diffraction analysis. The principal aim has been to evaluate pressure leaching kinetics of the material, under a range of experimental conditions that might have process potential. The parameters such as pressure, temperature, acid concentration, liquid/solid ratio and leaching time have been used to identify the optimum acid leaching of flue dust with highest copper and zinc leaching efficiency. Pressure acid leaching tests have been performed in a laboratory scale autoclave. The autoclave had a total volume of 2 l and it was loaded with 1.6 l of solution as the recommended batch size for such autoclaves is 80% of the capacity. Pregnant leach solutions, wash waters and residues have been analyzed for their copper, zinc and acid constituents to allow for stricter mass balances in each of the tests. The experimental results obtained show that using a solid/liquid ratio of 1/10, it was possible to leach more than 90% of copper and zinc after 2 hours, with a solution of 35 g/l H_2SO_4 at 110ºC temperature and 8 atm oxygen pressure.

Keywords: flue dusts, pressure leaching, copper, zinc

ИЗЛУЖВАНЕ ПОД НАЛЯГАНЕ НА ПРАХ ОТ ОЧИСТВАНЕ НА ДИМНИ ГАЗОВЕ: ЕКСПЕРИМЕНТАЛНО ИЗСЛЕДВАНЕ

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РЕЗЮМЕ. Представеното изследване е начална фаза на експериментална програма за определяне на възможността за използване на хидрометалургични техники при извличане на мед и цинк от прах, получен при очистката на димни газове. Димният прах се генерира като вторичен продукт при топенето на медни концентрати и съдържа основно метали като мед, цинк, желязо, арсен, кадмий и олово. Охарактеризирането на димния прах е извършено чрез химичен и рентгенов дифракционен анализ. Основната цел на изследването е да се оцени киселинното излужване под налягане при редица експериментални параметри като налягане, температура, концентрация на киселина, отношение твърдо/течно и време на излужване, и да се определят оптималните условия за достигане на най-високо извличане на медта и цинка. Киселинното излужване под налягане е проведено в лабораторен автоклав с ефективен обем 1,6 l, което е 80% от общия. Набогатените разтвори от излужването, промивните води и кековете са анализирани за мед, цинк и концентрация на сярна киселина, за да се направи пълен материален баланс на всеки експеримент. Резултатите от изследването показват, че е възможно да се излужат над 90% от медта и цинка при следните условия: отношение твърдо/течно 1/10, 35 g/l H_2SO_4, температура 110ºC, налягане на O_2 8 atm и контактно време 2 часа.

Ключови думи: димни прахове, излужване под налягане, мед, цинк

Introduction

Secondary sources can be considered as raw materials which have potentially high grade but also high complexity. Recovery of materials from secondary sources can be more difficult because the feed is less constant and homogeneous than in primary production. Several pyrometallurgical processes have been implemented for the treatment of secondary materials, however, these are generally only efficient for a constant composition feed and need to have a high production capacity to be economically viable.

Alternative hydrometallurgical routes to treating metallurgical wastes are therefore required (Liew, 2008). Pressure oxidation has been developed as a viable technology. It has found extensive commercial applications in mineral industry. Numerous pressure processing plants have been constructed worldwide for production of nickel, cobalt, copper and zinc from ores, concentrates and other metallurgical intermediates or secondary materials (Ozberk et al., 1995; Dreisinger, 1999; Evans, 1999; Collins et al., 2000).

Devnya Waste Treatment Plant (DWTP) will use a hydrometallurgical process route to treat a wide variety of metal-containing wastes. The investigation reported in this paper has been the initial phase of an experimental program to study the application of hydrometallurgical techniques to the recovery of copper and zinc from copper smelter flue dust. Flue dust is generated as a by-product of copper smelting operations and contains metals such as copper, zinc, iron, arsenic, cadmium, and lead. The composition of these dusts varies for different operations. The composition depends on the mineralogy of the concentrates, fluxes and circulating material (slag, dust, etc.), and their respective proportions.

The key unit operation envisaged in the Devnya Waste Treatment Plant (DWTP) is pressure oxidation leaching in autoclaves, where the copper and zinc are extracted into solution, lead is precipitate as lead sulfate and the precious metals are liberated conceivably for subsequent recovery. Before starting experiments on the pressure oxidation, a series of atmospheric leach tests with flue dust were performed to evaluate whether there was a response in copper and zinc extraction. Since the atmospheric leaching did not yield good results – very low copper and zinc recoveries, pressure leaching was initiated.

The amenability of the flue dust to the pressure oxidation process was evaluated in process development study, comprising batch tests, to assess the effects of parameters such as oxygen pressure, temperature, acid concentration, liquid/solid ratio and leaching time and to identify the optimum acid leaching conditions with highest copper and zinc leaching efficiency.

Materials and methods

The dust sample was collected during the smelting operation. The as-received sample was mixed thoroughly. Representative samples were subjected to chemical analysis, particle size analysis and X-ray diffraction (XRD).

Elemental composition

The composition of the sample was determined by Inductively Coupled Plasma Atomic Optical Emission Spectroscopy (ICP-OES) after the sample were digested in aqua regia. Table 1 presents the elemental analysis of the sample.

Table 1.
Elemental analysis of the flue dust

Element, unit	Value	Element, unit	Value
Au, g/t	5.40	Ni, g/t	227
Ag, g/t	205	Pb, %	15.07
As, %	1.03	Sb, g/t	798
Bi, %	2.05	Se, g/t	542
Cd, g/t	11100	Sn, g/t	2753.15
Co, g/t	18.3	Ta, g/t	0.10
Cu, %	27.4	Te, g/t	56.6
Fe, %	1.63	Zn, %	3.52
Ga, g/t	0.6	S, %	13.88

The analysis shows that the major metal constituents in the sample are copper, lead and zinc.

Particle size analysis

Screen analysis was conducted on the sample to assess the particle size distribution of the material. Results of the analysis show that the greatest percent of the sample was in the -0.5 +0.25 mm size fraction (Table 2).

Table 2.
Screen analysis of the flue dust

Sieve size, mm	Weight, g	Wt.% Ret.	Cum. Wt % Ret.	Cum. Wt % Pass
+1.0	34.54	6.9	6.9	93.1
-1.0 +0.5	52.76	10.6	17.5	82.5
-0.5 +0.25	376.6	75.5	93.0	7.0
-0.25+0.16	0.98	0.2	93.2	6.8
-0.16+0.09	24.2	4.9	98.1	1.9
-0.09+0.071	0.58	0.12	98.22	1.78
-0.071	8.95	1.8	100	
Total	498.61	100		

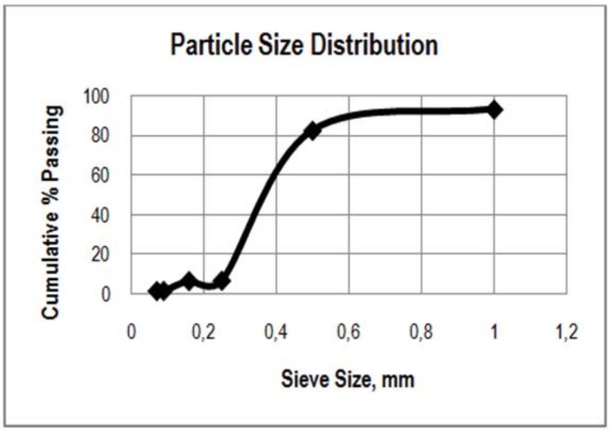

Fig. 1. Particle size distribution curve

From the cumulative curve (Figure 1), it can be seen that about 80% of the material was smaller than 0.5 mm.

X-ray diffraction (XRD) analysis

The mineralogy of the sample was determined by X-ray powder diffraction (XRD) with a Topas 4.2 (Bruker) software and PDF-2(2009) ICDD database. The diffraction pattern is shown on Figure 2. It can be seen that the main phases are poitevinite $(Cu,Fe)SO_4.H_2O$ – 30% and anglesite $PbSO_4$ – 30%. The other phases are bonattite $CuSO_4.3H_2O$ – 13%, cuprite Cu_2O – 2%, copper sulfate pentahydrate $CuSO_4.5H_2O$ – 9%, arsenolite As_2O_3 – 1% and moganite SiO_2 – 15%. Single phases of zinc, cadmium and bismuth were not identified. Cadmium and bismuth and certain amount of copper may be present in the anglesite.

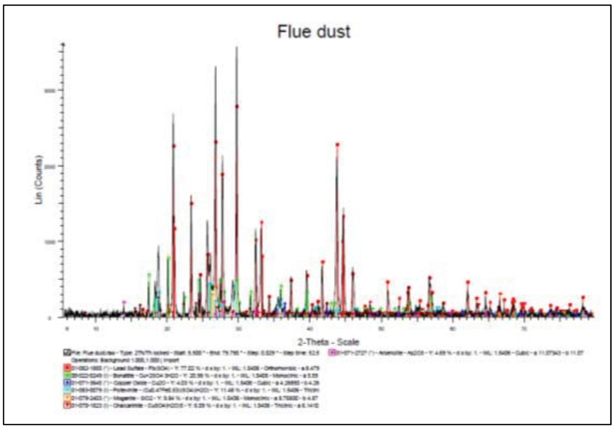

Fig. 2. X-ray diffraction (XRD) analysis of the flue dust

Pressure oxidation leaching

Batch pressure acid leaching tests with the flue dust have been performed in a laboratory scale autoclave. Experimental set-up is given in Figure 3. The autoclave had a total volume of 2 l and it was loaded with 1.6 l of solution as the recommended batch size for such autoclaves is 80% of the capacity. Pressure leaching examinations were performed using oxygen as an oxidant. At the end of the experiment, the pressure was relieved, the heater and the agitator switched off, and the flow of oxygen stopped. The reaction vessel was taken out and cooled rapidly by plunging it in cold water. The solution when cooled was filtered. The filtrate was collected, the residue was washed well with distilled water, and the wash water collected and analyzed. The residue was dried, weighed and a portion was analyzed. Chemical analyses were carried out by atomic absorption spectrometer (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) as well as by titration.

Results and Discussion

The experimental program was designed to investigate the influence on the flue dust sulfuric acid leaching of the following parameters - acid concentration, temperature, oxygen pressure and time of leaching. With this in mind, the experimental conditions were chosen so as to give the optimum results. The solid:liquid ratio was maintained at 1:10 and agitation speed - 650 rpm. The temperature of the process is dictated by the behaviour of sulfur during leaching. Temperatures of 90,100 and 110°C were chosen to maintain the temperature of reaction below the melting point of sulfur (119°C). Oxygen pressures of 6 and 8 atm were selected as being the optimum values from the data of other investigators. The initial sulfuric acid concentration was fixed at low value (35 g/l) in all of the experiments. The acid concentration was chosen to give a minimum required free acid of approximately 5 g/l of sulfuric acid in the autoclave discharge. Time of leaching was varied from 90 to120 minutes to give maximum extraction. Copper (Cu, %) and zinc (Zn, %) recovery results, calculated and based on chemical analysis of solutions and leach residue, are shown in Table 3 and Figure 4.

Table 3.
Experimental conditions and results of pressure leaching

Exp #	Temp, ^{o}C	pO_2, atm	Time, min	Cu, %	Zn, %
1	90	6	90	82.2	97.6
2	100	6	90	85.6	97.7
3	110	6	90	91.2	98.0
4	90	8	90	85.4	97.9
5	100	8	90	89.8	97.9
6	110	8	90	92.8	98.1
7	90	6	120	84.7	98.2
8	100	6	120	93.1	98.0
9	110	6	120	95.3	98.2
10	90	8	120	89.8	98.5
11	100	8	120	94.2	98.5
12	110	8	120	96.8	98.6

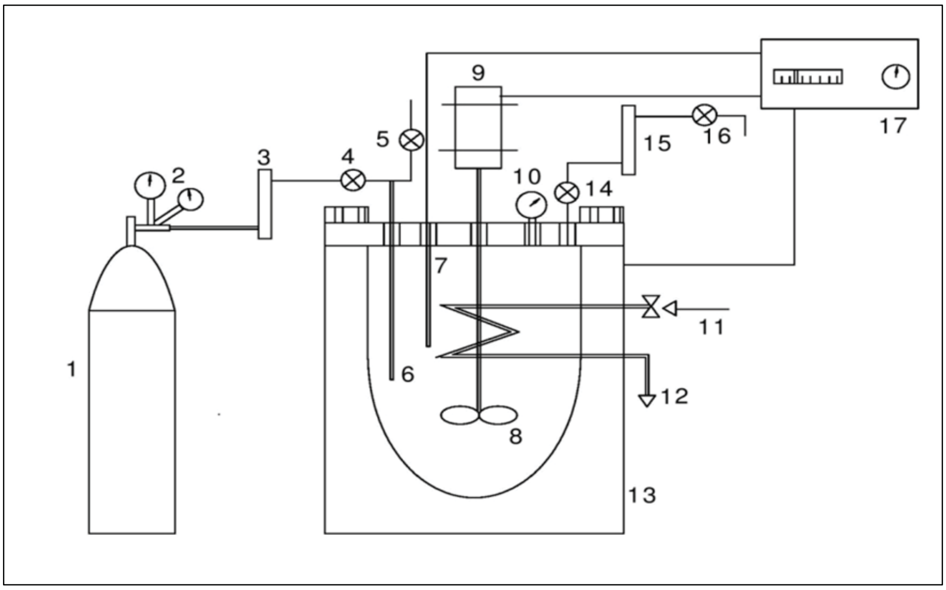

Fig. 3. Experimental set-up

1- Oxygen Gas Cylinder; 2 - Pressure Regulator; 3 - Gas Inlet Rotameter; 4 - Gas Inlet Valve; 5 - Sampling Valve; 6 - Gas Inlet; 7 - Temperature Sensor; 8 – Stirrer; 9 - Stir Motor; 10 - Pressure Gauge; 11 - Cooling Water; 12 - Water Drain; 13 - Heating Jacket; 14 - Gas Outlet Valve; 15 - Gas Outlet Rotameter; 16 - Pressure Control Valve; 17 – Controller.

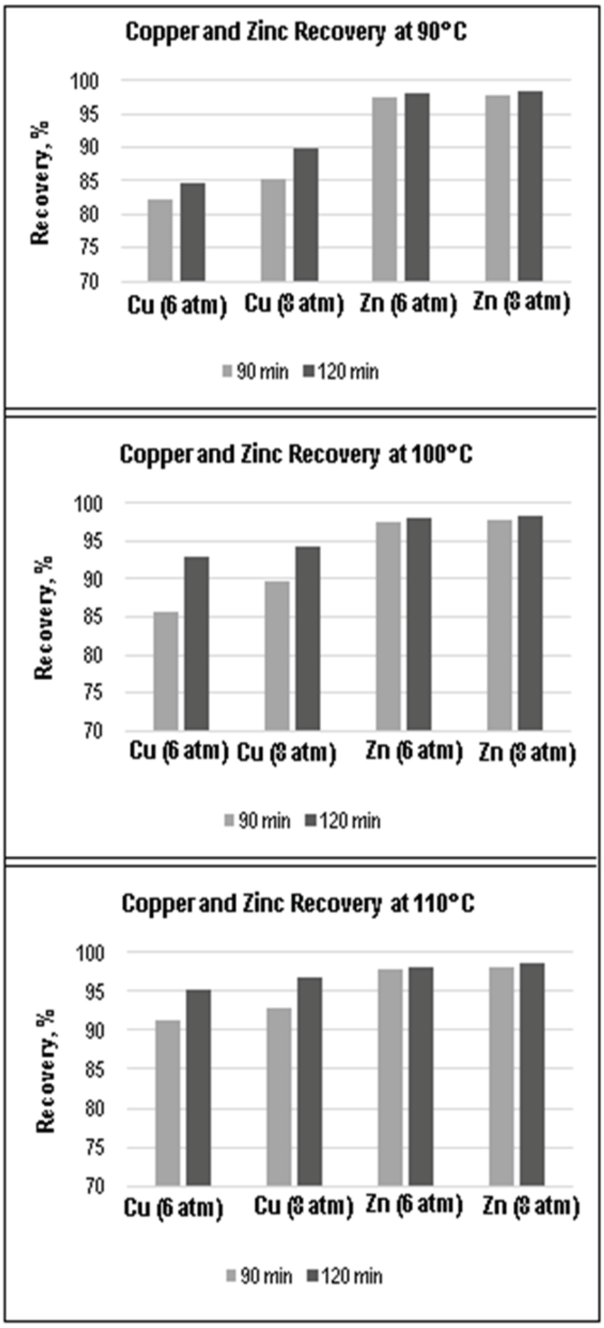

Fig. 4. Copper and zinc recoveries

As can be seen from the results, the pressure leach tests produce high copper and zinc recoveries at relatively low temperatures, medium oxygen pressures and short leaching times. The copper recoveries range from 82.2% to 96.8%, while the zinc recoveries range from 97.6% to 98.6%. The increase of temperature, oxygen pressure and leaching time leads to an increase in percent recovery of the two metals, particularly for copper. Copper and zinc recoveries reach their maximum of 96.8% and 98.6%, respectively at the temperature of 110°C, oxygen pressure of 8 atm and leaching time of 120 min.

Conclusions

The following conclusions, drawn from the results obtained from the experimental investigation, can be made:

- The recovery of copper and zinc from a flue dust, in an oxidative pressure-acid medium, is definitely viable with recoveries, higher than 95% in a leach time of 120 minutes.
- The rate of leaching, particularly for copper, increases with increasing temperature, oxygen pressure and leach time, with optimum conditions found to be at a temperature of 110°C, 8 atm oxygen pressure and a 120 minutes leach time.
- The recovery of the copper from the flue dust is much more dependent on the operating conditions than the recovery of the zinc.
- A solid:liquid ratio of 1:10 ensures fast leaching rate for the recovery of copper and zinc.
- An agitation rate of 650 rpm appeared to be adequate for oxygen dispersion, in order to ensure a fast reaction rate.
- An initial sulfuric acid concentration of 35 g/l produced low in acid base metals solution, is suitable for direct solvent extraction of copper.

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