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Extraction of Tin from Hardhead by Oxidation and Fusion with Sodium Hydroxide

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Abstract

In this research work, the extraction of tin from tin-iron alloy or hardhead which is the intermediate product obtained during tin smelting was investigated. The hardhead containing 32.40 wt% Sn and 45.81 wt% Fe was ground to different sizes and oxidized at 500 to 800 °C for 1 to 6 hours to form SnO_2 and Fe_2O_3. The results indicated that an increase in oxidation temperature decreased the required oxidation time. However using too high oxidation temperature (800 °C) resulted in sintering of the oxide product.In sodium hydroxide fusion stage, effects of fusion temperature, fusion time, NaOH quantity and oxide product size on tin leaching were investigated. By fusion the oxide product of -400+500 mesh size with 750 % excess NaOH at 700 °C for 2 hours in order to convert SnO_2 into soluble form of Na_2SnO_3,it was found that around 96 % of tin could be extracted by hot water (60°C) while the iron oxide remained in residues.

Keywords: Tin, Tin–iron alloy, Hardhead, Oxidation, Sodium hydroxide fusion, Leaching.

Introduction

Tin is widely used in several industries such as tinplates, solders, bronzes and so on. Almost tin metals are smelted from cassiterite concentrates by a conventional two stage-smelting process which is usually employed to extract tin from high-grade concentrates. The process consists of two main stages i.e. concentrate smelting and primary-slag smelting. In the first smelting stage, tin is smelted from the cassiterite concentrate by controlled reducing reaction to produce first slag for smelting in the next stage and crude tin metal containing less than 1% iron content. In the second smelting stage, the slag arising from the first stage is smelted to produce a discard slag of about 1% tin and tin-iron alloy called hardhead which can not be used and must be recycled in the smelting circuit. The recirculation of hardhead leads to decreased furnace capacity and increased energy consumption for smelting. Although sulfide fuming process can be applied for slag treatment without producing hardhead , it generates sulfur dioxide as a poisonous gas .[(1, 2)]

Extraction of tin from hardhead can be done by leaching with acid or alkaline solution. Potential-pH diagrams for the system tin-water and iron-water [(3)] show that tin would dissolve as either Sn^{2+} or Sn^{4+} and iron would dissolve as either Fe^{2+} or Fe^{3+} in acid solutions. Tin oxide would selectively dissolve as SnO_3^{2-} in alkaline solution whereas iron oxide would not dissolve. The leaching of hardhead in hydrochloric acid solution was investigated by S. Thongbo and C. Jarupisitthorn.[(4)] They found that tin was completely dissolved whereas 77 % of iron in the hardhead was extracted by 3 M HCl at 70 °C using 0.15 g/ml hardhead/acid solution within 6 hours. Separation of tin from the leached solution was done by pH adjustment with NaOH. At pH 3.0 around 97 % tin was recovered as tin hydroxide precipitate while iron remained in the solution. C. Jarupisitthorn, *et al.* [(5)] recovered tin from tin sludge which is waste from tinplate

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processing plant. The sludge containing approximately 30% tin in the forms of Na_2SnF_6 and $SnO_2 \cdot xH_2O$ was leached with 1.5 M NaOH at room temperature using 5% solid. They reported that around 97% tin was dissolved within 15 minutes. W.S. Jun, *et al.* [6] studied the dissolution of tin from pure tin metal and Sn-Fe alloys in sodium hydroxide solution using rotating disc. The experimental results showed that the dissolution rate of tin is approximately $8x10^{-9}$ mol/cm^{2}sec at 0.5 M sodium hydroxide concentration with air purging for oxidation. P. Veerothai[7] suggested that arsenic in tin-roaster dust containing 43.08% As and 5.77% Sn could be completely dissolved with sodium hydroxide solution while tin oxide in the roaster dust was not attacked, corresponding to the work of P. Yangyuen[8] which indicated that relatively low tin extraction from the roaster dust containing 55.84% Sn was obtained by alkaline leaching. However over 98 percent tin extraction could be achieved by sodium hydroxide roasting at 650 °C to form soluble tin prior to leaching. Also, Choosri, *et al.*[9] proposed a method to prepare zinc hydroxystannate ($ZnSn(OH)_6$) from cassiterite concentration (76.50% Sn) by fusion with NaOH at 700 °C, and then leached with 80 °C hot water. They found that cassiterite particle size greatly affected tin extraction. Using cassiterite of -300 mesh size to fuse with 300% excess NaOH, only 68.8% tin was recovered.

In this work tin extraction from hardhead was investigated by oxidizing the hardhead to form oxides according to reactions (1)and (2):

$$Sn\,(s) + O_2\,(g) = SnO_2(s) \quad (1)$$

$$4Fe\,(s) + 3O_2\,(g) = 2Fe_2O_3(s) \quad (2)$$

The oxide products were then fused with NaOH to form Na_2SnO_3 according to reaction (3):

$$SnO_2\,(s) + 2NaOH\,(l) = Na_2SnO_3\,(l) + H_2O\,(g) \quad (3)$$

Finally, tin in the form of Na_2SnO_3 was dissolved with distilled water leaving iron oxide unattacked.

Materials and Experimental Procedures

Materials

The hardhead used in this study was obtained from Thailand Smelting and Refining Co., Ltd. Its chemical composition was listed in Table 1. The X-ray diffraction pattern of the as-received hardhead shown in Figure 1 reveals the peaks of Sn and Fe.

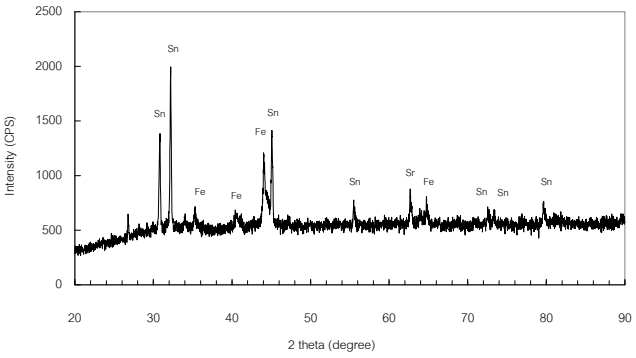

Figure 1. XRD pattern of the as - received hardhead.

Table 1. Chemical composition of hardhead (wt %)

H_2O	Sn	Fe	Ta_2O_5	Nb_2O_5	TiO_2	WO_3	S	As
0.47	32.40	45.81	0.9	1.4	1.3	4.2	0.31	0.06

Experimental Procedures

The hardhead was first ground to the predetermined sizes. For oxidation experiments, five grams of ground hardhead was placed in a porcelain crucible and then oxidized in an electric furnace heated at predetermined temperature under oxygen flow rate of 50 ml/min to aid the oxidation

process and the sample was weighed at a given time. For NaOH fusion experiments, five grams of the oxide product ground to different sizes were mixed with NaOH in the porcelain crucible and then fused in the electric furnace heated at a given temperature for a given time. Subsequent water leaching of the fused products was done in 500 ml hot water (60 °C) at 800 r.p.m. stirring speed for 2 hours. The leached liquor was sampled and analyzed for tin and iron by atomic absorption spectrometer to determine % dissolution.

Results and Discussion

Oxidation of Hardhead

Effect of oxidation temperature and time

The hardhead with -270 + 325 mesh size was oxidized at 500 to 800 °C up to 6 hours. As shown in Figure 2 the weight of the oxidized hardhead increased rapidly within the first hour of oxidation, afterwards the increment was relatively slow. The oxidation in the temperature range of 500 to 600 °C could not completely oxidize the hardhead within 6 hours whereas the oxidation done at 700 and 800 °C could oxidize the samples to constant weight at 5.92 g within 3 hours and 1 hour respectively but sintering of the oxide products resulted. It was found that crushing of the oxide product produced at 700°C could be done without difficulty.Therefore the oxidation temperature of 700°C was considered to be optimum.

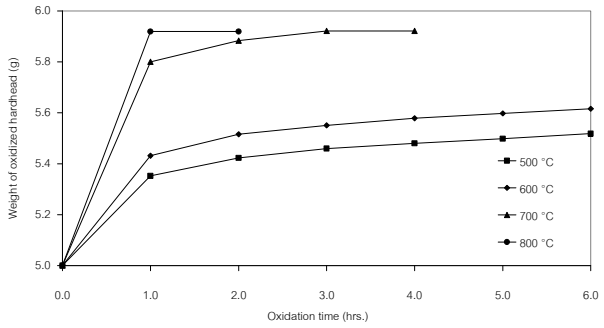

Figure 2. Effect of oxidation temperature on the oxidation of hardhead (hardhead size -270+325 mesh)

Effect of Hardhead size

The effect of hardhead size on weight gain of the oxidized hardhead was conducted at 700 °C. As presented in Figure 3 the hardhead of -150+200 mesh size could not be completely oxidized within 6 hours while finer hardhead sizes of -270+325 mesh and -325+400 mesh could be completely oxidized within 3 hours and 1 hour respectively.

The XRD analysis of the oxide product shown in Figure 4 indicated that Sn and Fe in the hardhead were converted into SnO_2 and Fe_2O_3.

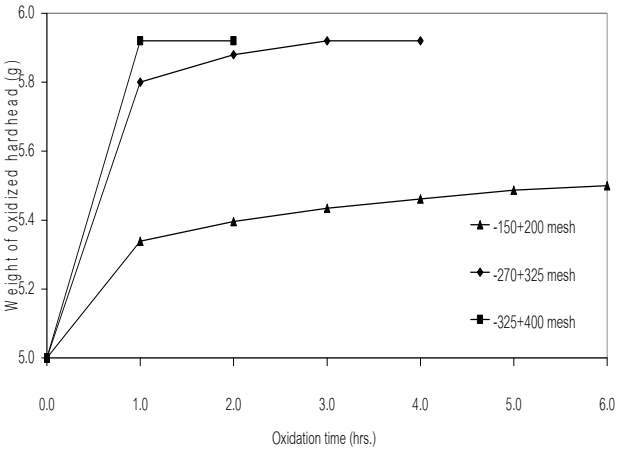

Figure 3. Effect of hardhead size on the oxidation of hardhead (oxidation temperature: 700 °C)**.**

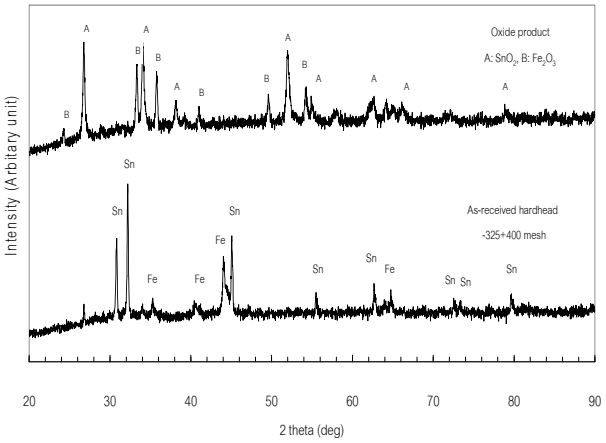

Figure 4. XRD pattern of the as - received hardhead and the oxide product obtained from oxidising hardhead at 700 °C for 2 hours.

Fusion of Oxide Product with Sodium Hydroxide

Effect of Fusion Time

The oxide product was ground to -325+400 mesh size, then mixed with 250% excess NaOH and fused at 500 °C to study the effect of fusion time on tin leaching. As shown in Figure 5 tin dissolution increased with fusion time. When fusion time increased from 15 to 30 minutes, the dissolution of tin increased from 19.6 to 22.0%. Increasing fusion time further to 1 and 2 hours increased tin dissolution insignificantly. Most of the iron in the fused product was not dissolved and remained in the residue. Hence tin and iron can be separated. The results indicated that the fusion time of 2 hours should be sufficient for SnO_2 to react with NaOH according to the reaction (3).

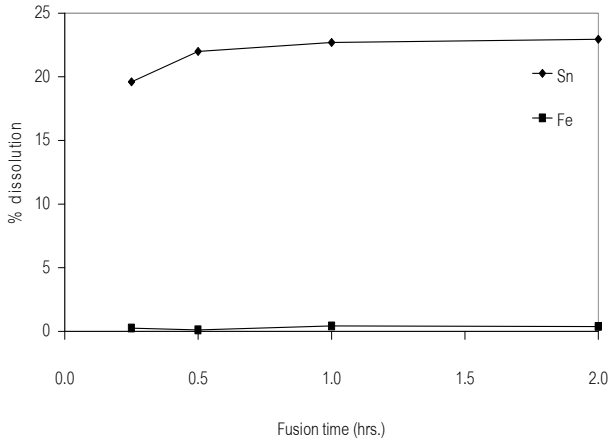

Figure 5. Effect of fusion time on the dissolution of tin and iron (oxide product size: - 325 + 400 mesh, fusion temperature : 500°C, NaOH quantity: 250% excess)

Effect of Fusion Temperature

Figure 6 shows the effect of fusion temperature on tin and iron dissolution. With higher fusion temperature more tin can be extracted. Increasing fusion temperature from 500 to 700 °C leads to increased tin dissolution from 22.9% to 35.5%. Percent tin dissolution obtained here is much lower as compared to the work of Yangyuen.[8] This may be attributed to the significant effects of other parameters such as NaOH quantity and particle size since the fusion temperature employed was relatively close.

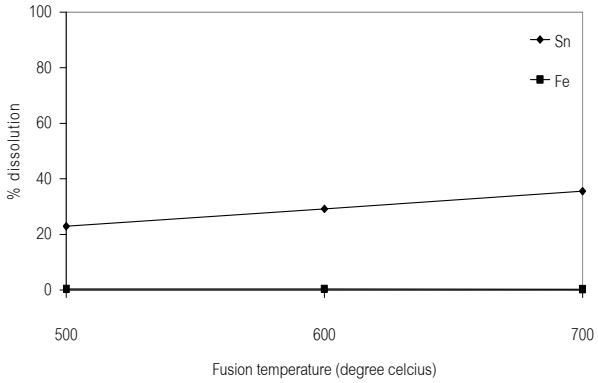

Figure 6. Effect of fusion temperature on the dissolution of tin and iron (oxide product size: - 325 + 400 mesh , NaOH quantity: 250 % excess, fusion time : 2 hours)

Effect of Sodium Hydroxide Quantity

Figure 7 illustrates the effect of sodium hydroxide quantity on tin leaching. It can be seen that percent tin dissolution increases from 35.5% for 250% excess NaOH to 62.7% for 750% excess NaOH. This figure is comparable to 68% tin extraction as reported by Choosri, *et al.*[9] who conducted experiments on the extraction of tin from cassiterite concentrate with -300 mesh particle size using 300% excess NaOH at 700 °C. As initial tin content in the hardhead used in this study is much lower than that in the cassiterite concentrate (76.5% Sn). Therefore much excess NaOH is necessary for thorough mixing of the samples. Still percent tin dissolution is much lower as compared to the work of Yangyuen, [8] who reported over 98% tin in roaster dust extracted using around 110% excess NaOH for fusion. Very fine roaster dust is expected to respond well to mixing and reacting with NaOH. Therefore, the effect of oxide product size was investigated in later experiments.

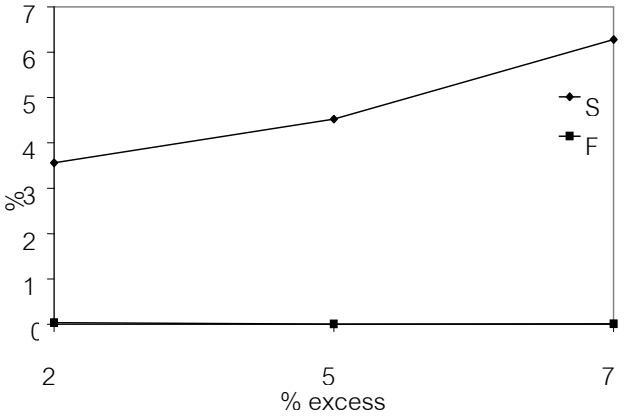

Figure 7. Effect of NaOH quantity on the dissolution of tin and iron (oxide product size : - 325 + 400 mesh , fusion temperature: 700 °C, fusion time: 2 hours)

Effect of Oxide Product size

Figure 8 shows that the oxide product size is an important parameter affecting the tin leaching. The tin dissolution increased from 45.2% to 78.1% with 500% excess NaOH and increased from 62.7% to 96.6% with 750% excess NaOH as the result of reducing the oxide product size from -325+400 mesh to -400+500 mesh. The tin dissolution of 96% is considered to be optimum in this investigation.

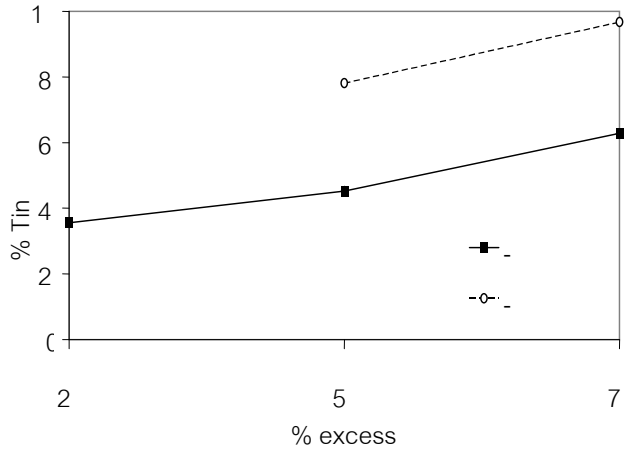

Figure 8. Effect of oxide product size on tin dissolution at various NaOH quantity.

Conclusions

Extraction of tin from hardhead containing 32.40%Sn can be achieved by two main steps consisting of oxidation of the hardhead and fusion the oxide product with NaOH. The results can be concluded as follows:

1. The hardhead size used in the oxidation process must be fine enough , namely -270 mesh and the oxidation should be conducted at 700 °C for 3 hours to achieve fully oxidized products. For finer hardhead, such as -325 mesh, the required oxidation time is up to 1 hour.

2. The oxide products must be ground to -400 mesh prior to mixing with 750% excess NaOH and fused at 700 °C for 2 hours to obtain soluble tin.

3. Around 96% tin could be selectively extracted leaving the iron remained in the residues in this study.

Acknowledgements

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