RECOVERY OF METAL VALUES FROM JOS TIN SLAG USING NaOH

FERGUSON H. TOBINS and NICHOLAS C. OFORKA

(Received 1 December 1999; Revision accepted 22 May, 2000)

ABSTRACT

The recovery of metal values from Jos tin slag using NaOH was investigated. Various concentrations of NaOH (0.5M, 1.0M, 2.0M, 5.2M, 3.0M, 3.5M and 4.0M) were used to leach the slag. The leaching was done at 400°C. Various grades of slag were used and designated as samples A, B, C, D and E. It was observed from the figures that the least recovery of tungsten from the slag (less than 50% from sample A) was with 0.5M of NaOH. However, 4.0M of NaOH recovered about 98.7% of tungsten. The trend was the same for all the samples used, that is, the more the concentration of the NaOH, the higher the percentage recovery of tungsten from the tin slag. This is because oxidizing alkaline attacks tungsten energetically. This method is therefore a very good starting point to recover tungsten metal from the slag.

Keywords: Leaching, recovery, extraction, Tin slag.

INTRODUCTION

The mineral processing and metal extraction industries have a readily perceptible effect on the environment - inevitably at the plant site and potentially at locations away from the site. It is increasingly less acceptable for any individual, corporation or industry, to make others pay the costs of environmental pollution. Meeting environmental regulations demands the efficient use of process effluents or wastes. Since these former wastes streams often contain metal values, an environmentally driven waste treatment process may provide a marketable by - product that helps reduce waste treatment costs. There are numerous examples of successful attempts to recover values from astes (Edwards, 1991).

When Henderson (1964) used carbon as a reducing agent for the chlorination of Scheelite tungsten recoveries of approximately 95% were achieved at 500°C to 700°C. Additions of calcium fluoride to scheelite in a ratio of 5:16 increased tungsten recovery at 600°C from 65 to 99%. Kablukou et al (1988), used X-ray diffraction, Scanning Electron Microscope

(SEM) and Infra Red (IR) spectrometry to analyze the chemical composition of tin smelting slags. They concluded that the highest recovery of tungsten could be achieved by the application of high-temperature melting with a Na containing flux. On the other hand, Sobol et al (1990) looked at the hydrothermal alkaline leaching of tungsten from tin smelting slags. Korotaeva et al (1990) investigated the recovery of tungsten from tin slags containing 3 - 4% W. The leaching of slag was done with carbonate and fluoride in an autoclave at temperatures between 200°C and 225°C resulting in tungsten yield of nearly 100%.

Very little has been reported on the chlorination of tungsten minerals as a method of extracting tungsten (Henderson, 1964). Henderson in his work, recovered tungsten from the mineral scheelite as a volatile chloride from reactions involving scheelite, chlorine and a reducing agent.

Tin slag is one of the numerous metallurgical wastes in Nigeria. It contains tungsten among other valuable metals (Kock and Paschen, 1989; Tobins 1997). Tungsten is a very valuable alloying element especially

in the production of tool steel. Its production therefore is of relative economic importance for this country as well as enhance the production capacity of such alloys locally. In this present work, the recovery of tungsten from tin slag by leaching with NaOH has been investigated.

MATERIALS AND METHODS

The tin slag was supplied by the Makeri Smelting Company Jos, Nigeria in five sample bags as follows.

Table 1 Description of Slag

- Control of Sing					
Slag sample	Sample				
	Code				
No 1 slag	\mathbf{A}'				
Lump slag	В				
Final slag	C				
Final head Slag Fines	D				
Final head slag oversize	E				

These slag samples were ground and analyzed to determine the constituent elements, the results of which are given in Tables 2.

5.00g of each sample (-150μm) was leached at 400°C and atmospheric pressure using sodium hydroxide. The concentration of NaOH used was varied from 0.5M to 4.0M. The leaching was carried out by digesting each sample in 100ml of NaOH. The set up was agitated or stirred for 20min at the end of which filtrate was collected. Elemental analysis was carried out using Atomic Absorption Spectrometer. The results obtained are given in Table 3.

RESULTS AND DISCUSSION

Table 2 shows the results of the analyzed samples. The %Fe in the slag is highest in

Table 2: Constituents of the Slag

Sample	%Fe	%Sn	%Nb	%Ta	%Ti	%W
Ą	26	17	2.5	5.9	4.6	6.9
В	25	21	3.6	5.8	5.2	7.9
C	14	4	3.9	6.0	7.1	8.5
D	20	29	5.9	6.2	6.6	9.7
E	15	10	7.0	6.7	7.8	10.4

Table 3: The effect of Leaching the Tin slag with NaOH.

Leaching of Sample A								
NaOH Concentration (M)	%W	%Та	%Ti	%Nb	%Fe			
0.5	45.5	0.2	0.9	0.0	0,4			
1.0	47.0	0.4	1.8	0.0	0.04			
2.0	49.8	0.8	4.6	0.0	0.06			
2.5	68.7	1.2	4.8	0.0	0.2			
3.0	75.2	1.6	5.0	0.0	0.2			
3.5	88.8	o 1.4	5.2	0.1	0.3			
4.0	98.7	0.2	0.3	0.1	0.4			

Leaching of Sample B

		Sumpic D			
NaOH Concentration (M)	%W	%Та	%Ti	%Nb	%Fe
0.5	30.0	4.7	8.9	0.0	0.06
1.0	48.0	4.7	8.9	0.0	0.06
2.0	48.0	7.0	10.2	0.0	0.05
2.5	59.2	8.1	10.6	0.0	0.12
3.0	78.3	8.4	10.9	0.0	0.13
3.5	90.6	3.8	11.2	0.0	0.16
4.0	97.8	1.1	0.5	0.0	0.17

Leaching of Sample C							
NaOH Concentration (M)	%W	%Ta	%Ti	%Nb	%Fe		
0.5	34.5	17.3	0.0	.0.0	0.2		
1.0	39.8	16.6	0.0	0.0	0.2		
2.0	45.7	18.2	0.0	0.0	0.3		
2.5	61.1	10.1	0.0	0.0	0.4		
3.0	78.0	3.4	0.0	0.0	0.3		
3.5	94.3	1.9	0.0	0.0	0.2		
4.0	98.2	0.8	0.0	0.0	0.2		

Leaching of Sample D								
NaOH Concentration (M)	%W	%Ta	%Ti	%Nb	%Fe			
0.5	37.3	17.7	0.0	0.0	0.1			
1.0	41.0	18.2	0.0	0.0	- 0.1			
2.0	43.5	18.6	0.0	0.0	0.2			
2.5	63.2	16.7	0.0	0.0	0.2			
3.0	77.6	10.1	0.0	0.0	0.2			
3.5	89.3	3.1	0.0	0.0	0.2			
4.0	96.9	1.2	0.0	0.0	0.2			

Leaching of Sample E							
NaOH Concentration (M)	%W	%Ta	%Ti	%Nb	%Fe		
0.5	42.5	16.8	0.0	0.0	0.1		
1.0	45.0	17.7	0.0	0.0	0.2		
2.0	46.0	18.6	€.0	0.0	0.4		
2.5	59.6	13.2	0.0	0.1	0.2		
3.0	79.4	10.2	0.0	0.0	0.2		
3.5	88.9	4.3	0.0	0.0	0.2		
4.0	98.1	1.0	0.0	0.0	0.3		

sample A (26%) and least in sample C (14%). From the results obtained, there is a lot of Sn in sample D (29% Sn) whereas sample C contains only 4% Sn. The %Nb in the slag increases with slag number. Sample A contains 2.5% Nb while sample E contains 7.0% Nb. The slag contains an average percentage of 6.0% Ta. Sample A contains 4.6% Ti which increases to 7.8% Ti in sample E after dropping to 6.6% Ti in sample D. The %W increases from sample A (6.9%) to 10.4% W for sample E.

It is clear from this result that the final slag oversize has the least percentages of Fe (15%) and Sn (10% Sn), whereas the percentage of the valuable metals in the slag (Nb, Ta, Ti and W) increases at the later stages of the smelting operation. The final slag oversize contains the highest percentage of each of these valuable metals (7.0% Nb, 6.4% Ta, 7.8% Ti and 10.4% W). This confirms the fact that these metals are enriched in the tin

slag during the smelting operation (Borchers et al, 1981).

Table 3 (sample A to E) shows the results of the leaching of the slag samples with various NaOH concentrations. Figures 1, 2, 3, 4 and 5 show the graphs of percentage of element extracted after leaching against the various concentrations of the NaOH used for the leaching. It is very clear from the graphs that the percentage of tungsten extracted increased with the concentration of NaOH used for the leaching. The percentages of the other elements are almost zero. In Figure 1 for instance, 0.5M of NaOH yielded less than 50% tungsten, while 4.0M of NaoH extracted between 98% and 99% tungsten. The recoveries of tantalum (Ta), titanium (Ti), niobium (Nb) and Iron (Fe) were well below Iron and Niobium were not even extracted by the NaOH, since their percentage recoveries were zero irrespective of the concentration of NaOH.

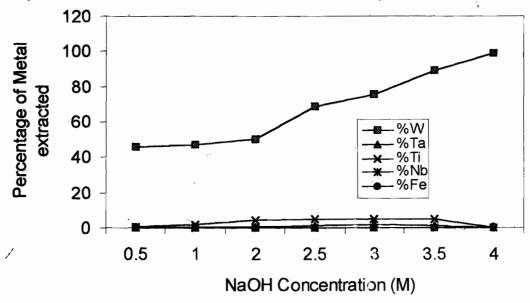


Figure 1. The effect of Leaching the Tin Slag with NaOH (Sample A)

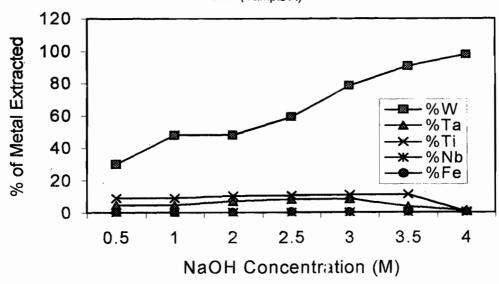


Figure 2. The Effect of Leaching the Tin Slag with NaOH (Sample B)

From Figures 2, 3, 4, and 5, it can be seen that the highest recovery of tungsten was recorded using 4.0M of NaOH, for all the samples of the slag used, while the least recovery was obtained using 0.5M of NaOH. The reason for this trend is that soda potassium nitrate melts and other oxidizing alkaline melts attack tungsten energetically. Again tungsten ores, after a preliminary concentration by mechanical and electromagnetic ore dressing processes, are attacked by fusion with soda in a reverberatory furnace (Tobins, 1997).

 $2FeWO_4 + 2Na_2CO_3 + \frac{1}{2}O_2 = 2Na_2WO_4 + Fe_2O_3 + 2Co_2.$ This explains why the more the concentration

of NaOH, the more the percentage recovery of tungsten from the tin slag. This method is therefore unsuitable for the recovery of valuable metals such as titanium, niobium and tantalum from the tin slag.

CONCLUSION

Tungsten, W can be extracted from the Jos tin slag when leached with 4M NaOH. From the figures, it is very clear that the least recovery of tungsten from the slag (less than 50% from sample A) was obtained when 0.5M of NaOH was used for the leaching. However, with 4.0M of NaOH there was an increase in

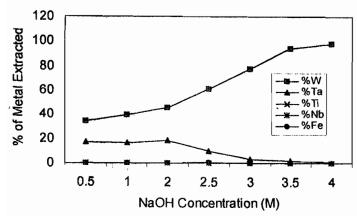


Figure 3. The Effect of Leaching the Tin Slag with NaOH (Sample C)

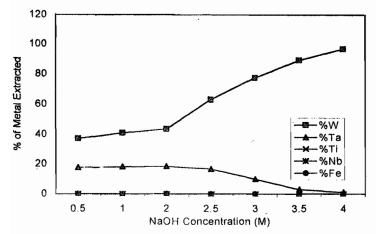


Figure 4. The Effect of Leaching the Tin Slag with NaOH (Sample D)

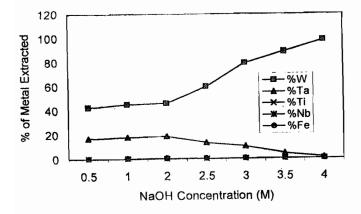


Figure 5. The Effect of Leaching the Tin Slag with NaOH (Sample E)

the percentage of tungsten recovered, up to about 98.7%. Thus, more the concentration of the NaOH, the higher the percentage of recovery of tungsten from the tin slag. This trend was observed for all the samples of tin slag

used. Oxidizing alkaline attacks tungsten, so the more the concentration of NaOH the more the amount of tungsten extracted.

This method is not suitable for the recovery of other valuable metals like niobium, titanium and tantalum. The methods used for the recovery of these metals from tin slag are discussed elsewhere (Tobins, 1997). This is a very good starting step for the recovery of tungsten metal from tin slag. It is recommended therefore that more work should be done in this direction to recover tungsten metal from the tin slag starting with the leaching with 4M NaOH.

Acknowledgement

The authors are very grateful to NUC/World Bank for the grant that enabled one of the authors to carry out the experimental work at the University of Leeds, England. We are also grateful to Dr. R. V. Kumer of the same university for his assistance.

REFERENCES

•Borchers, P.K., George, J.K. and Goslar, S.H.C. 1981. Extractive Metallurgy of Tantalum. Conference Proceedings of TMS of AIME: 107-126.

Edwards, C.R., 1991. The recovery of metal Values from process residues. Journal of Metals 43(6): 32 – 33.

Henderson, A.W. 1964. Chlorination of ore and concentrates as applied to extracting tantalum, columbium and tungstem. Journal of Metals. 4(2) pp. 155 – 160.

Kablukov, V.I., Mashov, V.I. and Dulepov, E.W., 1988. Chemical Composition of tin production slags and tungsten speciation in them. Kompleksm, Ispol'z. Miner. Syr'ya 7:52-54.

- Kock, W. and Passhen, P., 1989. Tantalum – Processing, Properties and Applications. Journal of Metals, 41(10): p. 33.
- Korotaeva, Z.A., gol'dberg, E.L. and Dugel'nyi, A.P., (1990). Recovery of tungsten from waste of Novosibirsk tin plant Izv. Sib. Otd. Alacad. Nauk SSSR, Ser Khion Nauk (5): 112 115.

- Sobol, S.L., Gornshtein, A.D. Morozov, V.A. and Bulavina, I.P. 1990. Hydrothermal alkaline leaching of tungsten from Tin manufacturing slags. TsVetm. Met., (11): 75-79.
- Tobins, F.H. 1997. Recovery of valuable metals from wastes (Tin slag and tin plated cans) Ph.D Thesis, University of Port Harcourt, (Unpublished) 177 p.