

CR PROCESS FOR TREATING COMPLEX TIN DUSTS CONTAINING HIGH ARSENIC AND ANTIMONY^①

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ABSTRACT

A new process for treating complex tin dusts containing high arsenic and antimony—CR chlorination-dry-distillation process (here after, CR process) has been described. The key step of this process is the CR distilling arsenic process in which the tin dusts are leached with a medium concentration hydrochloric acid. A metal or a metallic sulfide is used as a reducing agent to reduce As(V) and Sb(V), and arsenic trichloride is simultaneously distilled from the leaching system. Then arsenic is precipitated for regenerated hydrochloric acid with the sulfide precipitation method. The prominent characteristics of the CR process are of great advantage in removing impurities such as Pb, As, Zn and Sb from the dusts in one step, recovering all valuable elements, eliminating the arsenic harm, and the consequent metallurgy of tin.

Key words: metallurgy of tin chlorination metallurgy distillation arsenic harm

1 INTRODUCTION

Development and application of the complex tin ores are of great significance because of rapidly decreasing tin reserves and rapidly increasing requirements for them^[1-3]. The ore of a large alluvial tin mine in western Guangxi is a refractory tin oxide ore accompanied by polymetallic elements Pb, Sb, As, Zn, etc. A medium tin concentrate containing 5% Sn is concentrated for fuming to produce complex tin dusts containing 20% Sn and high contents of impurity elements, i. e. As, Zn, etc (see Tables 1 and 2). Though Li, Wangchang^[4] and Hu, Liuxuan^[5] did much investigation on technologies for treating the tin dusts and obtained good results, there are still many problems such as arsenic pollution and the difficulty of operating vacuum distillation equipment at high temperature. Consequently, it is

of great importance to find a new process for treating the complex tin dusts.

Table 1 The chemical analysis of the complex tin dusts

Elements	Sn	Sb	Pb	Zn	Ag	S	Fe
wt.-%	23.28	11.81	20.74	4.79	0.055	2.58	1.85
Elements	Bi	As	In	SiO ₂	CaO	Al ₂ O ₃	
wt.-%	0.004	6.42	0.047	2.79	0.81	1.20	

2 SELECTION OF TECHNOLOGICAL FLOW-SHEET

Based on the chlorination-dry-distillation process^[6], volatilization characteristics of arsenic trichloride and the use of chlorination distillation for extracting germanium^[7], a principle technology flow-sheet CR process has been selected for treating this polymetallic complex tin dusts (Fig. 1). Its characteristics are lower arsenic removal temperatures, a lower requirement for the amount of reducing agent needed for both arsenic and antimony removal,

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and the direct production chemicals from recovered elements.

Table 2 The phase analysis of the complex tin dusts

Tin	Sn in SnO	Sn in SnO ₂	Sn in SnS	ΣSn	
Phase / %	1.28	19.68	1.40	22.34	
Antimony	Sb in Sb ₂ O ₃	Sb in Sb ₂ S ₃	Sb in M ₃ (SbO ₄) ₂	ΣSb	
Phase / %	2.59	0.52	8.87	11.98	
Lead	Pb in PbSO ₄	Pb in PbO	Pb in PbS	Pb in insoluble residue	ΣPb
Phase / %	5.11	11.77	1.12	2.39	20.39
Arsenic	As in As ₂ O ₃	As in M ₃ (AsO ₄) ₂	As in As ₂ S ₃	As in As ₂ S ₃	ΣAs
Phase / %	2.07	3.68	0.12	0.53	6.40

3 EXPERIMENTAL METHODS

The theoretical amount of hydrochloric acid was calculated, and the theoretical amount of reducing agent was calculated in light of the amounts of high valence As and Sb, since the contents of original metal sulfides (MeS) should be reduced. The feeding methods for

the reducing agent and the choice of chlorination-leaching systems are also important.

The experimental conditions (see Table 3) were ranged with normal table of $L_{16}(5^4)$. There is a temperature deviation of $\pm 1^\circ\text{C}$ in the experiments on a scale of 30 g dust per unit time.

Table 3 The rangements of the tin dusts chlorination-leaching distilling arsenic experimental conditions

Systems level	Factors				
	A	B	C	D	E
	HCl / ml	acid concentration / molL ⁻¹	deviation	the ratio of adding MeS to original MeS	leaching time / h
1	60	6	/	0.884	2
2	80	8	/	1.010	3
3	100	10	/	1.26	4
4	120	12	/	1.324	5

4 EXPERIMENTAL RESULTS AND DATA TREATMENTS

Experimental data for the arsenic chlorination-leaching distillation process for the HCl-

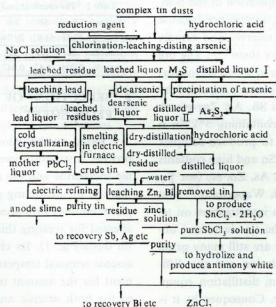


Fig. 1 The principle technology flow-sheet of CR process for treating complex tin dusts

NaCl-H₂O system have been calculated with a computer to obtain the square deviation analysis results shown in Table 4. S, f, and V represent the variations of deviations, freedoms, and mean variations respectively. F is the F-test (variance test ratio). They are all derived from the relative expressions in reference [8].

Table 4 shows that Factor A is notably effective on the distillation of arsenic, and is more effective on the removal of lead and zinc. Factor B is notably effective on the removal of zinc and the distillation of arsenic and is more effective on the removal of lead. Factor D is especially effective on the removal of antimony and zinc, and notably effective on the removal of arsenic and the recovery of tin in residues. Factor E is only notably effective on the recovery of tin in residues.

After all targets synthesized, the optimum levels are listed in Table 5. It shows that the optimum levels of factors A and E are respectively A₄ and E₃. There is a discrepancy between the optimum levels of factor B from the view point of the removal of lead and other targets, and there is also a discrepancy between the optimum levels of factor D for removing antimony and other targets. In order to solve the first discrepancy, the arsenic chlorination-leaching-distilling process is conducted in the system without NaCl, and then the lead is removed from leached residues separately. The second discrepancy may be solved by adding reducing agent in batches. Consequently, the optimum conditions are chosen as A₄B₃D₃E₃.

According to the analysis of the experimental results in the Me-HCl-H₂O leaching system, the comparison experiments of MeS and HCl in batch and batches respectively were carried out. The results show that 2 h is enough for reducing high valence antimony; 0.122 g MeS per 1g dusts is the best amount for the second batch. In the case of adding MeS in one batch the removed arsenic is great-

ly decreased. However, in the case of adding reduc agents in batches, the removed arsenic is almost unvarying and the removed antimony is also high, which is enough to prove the importance of adding reducing agent in batches.

Table 4 The square deviation analysis of the data from arsenic chlorination-leaching-distilling experiments of tin dusts in the system of HCl-NaCl-H₂O

targets	factors	square deviations			F	significance probability	notice
		S	f	V			
Removed antimony	A	27.09	3	9.03	—		
	B	77.34	3	25.78	3.40	*	F _{3,12} (3,6)
	D	932.63	3	310.88	40.99	*	= 9.78
	E	59.33	3	19.78	2.61		S ² = S ₁ + S ₂
	C	18.42	3	6.14	—		
	deviation ^a	45.51	6	7.58	—		
Removed arsenic	A	32.16	3	10.72	—		
	B	76.65	3	25.55	2.132		
	D	164.66	3	54.89	4.58	*	S ² = S ₁ + S ₂
	E	38.45	3	12.82	—		
	C	37.25	3	12.42	—		
	deviation ^a	107.86	9	11.98	—		
Removed lead	A	667.84	3	222.61	5.573	*	
	B	618.04	3	206.01	5.157	*	F _{3,12} (3,9)
	D	159.34	3	53.11	—		= 3.86
	E	88.37	3	29.46	—		S ² = S ₁ + S ₂
	C	111.79	3	37.26	—		
	deviation ^a	359.50	9	39.94	—		
Removed Zinc	A	36.09	3	12.03	6.69	*	
	B	64.87	3	21.62	12.03	*	
	D	83.55	3	27.85	15.49	*	F _{3,12} (3,6)
	E	6.49	3	2.16	—		= 4.76
	C	4.29	3	1.43	—		S ² = S ₁ + S ₂
	deviation ^a	10.79	6	1.80	—		
distilled arsenic	A	2981.16	3	993.72	18.59	*	
	B	4020.81	3	1340.27	25.07	*	
	D	514.98	3	171.66	3.21		S ² = S ₁ + S ₂
	E	125.70	3	41.90	—		
	C	195.08	3	65.03	—		
	deviation ^a	320.77	6	53.46	—		
Recovery of tin in residues	A	8.08	3	2.69	—		
	B	4.84	3	1.61	—		
	D	34.96	3	11.65	4.70	*	S ² = S ₁ + S ₂
	E	31.71	3	10.57	4.72	*	S ₁ + S ₂
	C	9.38	3	3.13	—		
	deviation ^a	22.295	9	2.477	—		

Finally, the synthetic condition experiments have been carried out to obtain the most significant results (see Tables 6 and 7).

Table 5 The synthetic analysis of the optimal levels in the system of $\text{HCl-NaCl-H}_2\text{O}$

Factors	Removed				Distilled		Recovery of tin in residues
	Sb	As	Pb	Zn	As	Cl	
A	0	0	4	4	4	2	0
B	3	4	1	3	3	3	0
D	3	1	0	1	1	1	1
E	3	3	0	0	4	0	3

notice, 0 indicates that any level may be well.

Table 6 The removed and distilled impurity elements and the recovery of tin in residues (%)

Sample	No	rem.	elements							
			Sn	Sb	As	Pb	Zn	S	Fe	Ag
F-78		oved	85.68*	95.66	96.74	98.39	93.85	84.99	88.64	98.66
F-101			78.54*	88.38	97.76	98.21	98.64	-	-	-
		Distilled	0.106	1.68	95.35	-	-	-74.78	-	-

* recoveries in residues.

Table 7 The chemical components of leached lead residues (tin concentrates) and leached liquors (% or g / L)

Items	Sample No	elements								
		Sn	Sb	As	Pb	Zn	Fe	Ag	S ₂	Ca SiO ₂
tin concentrates	F-76R	49.32	4.04	0.95	0.97	1.59	-	0.0128	-	-
	F-78R	49.42	2.61	0.54	0.86	0.76	0.49	0.0019	1	7.65
leached liquors	F-78L	3.76	32.11	0.33	1.16	33.62	4.85	0.133	5.48	1.09
	F-99L	3.03	23.6	0.39	1.16	41.36	5.79	0.081	4.21	1.00

5 DISCUSSION

In the case of adding MeS in one batch, the effects of MeS on As and Sb removal are notable, the results are antagonistic. Because the original metallic sulfides in the tin dusts are enough for reducing the high valence arsenic and the reduced arsenic introduced into the leaching solution reacts with H_2S or MeS to produce As_2S_3 before it volatilized out of the leaching system, the more MeS added, the more the As_2S_3 produced and the less the ar-

senic removed. In contrast, the more MeS added, the higher the valence antimony reduced and the more the antimony removed. The above discrepancy was solved by adding MeS in batches, because the amount of MeS added first with the tin dusts is less, so that the amount of MeS is only enough to reduce high valence As resulting in production of only a slight amount of H_2S . Therefore, the high valence arsenic is reduced and is introduced into the leaching solution and distills continuously from the leaching system. When the second batch of MeS is added, a great amount of As has been evaporated and removed from the reactive system, and MeS is mainly used for reducing high valence antimony. Consequently, the removal efficiencies of antimony are very high.

The distilled As and Cl increased rapidly with increasing amounts and concentrations, of hydrochloric acid. It is apparent that the higher acid concentration increases the vapor pressure of AsCl_3 and HCl , and the larger amount of acid extends the time for holding the vapor pressures. Therefore, high concentrations and large amounts of acid are required for distilling arsenic fully. The effects of amount and concentration of the acid on the removal of lead are notable, and the effects of the liquid to solid ratio on lead dissolved in the leaching solution are substantial. As a matter of fact, greater the amount of acid, the higher the ratio of liquid to solid is. When the amount of acid is held constant, the lower the acid concentration and the higher the ratio of liquor to solid are, the greater the amount of lead dissolved will be. Consequently, there is a discrepancy between the requirements for the removal of lead and the distillation of arsenic with regard to acid concentration. The arsenic chlorination-distilling process conducted in a

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