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SMELTER FUME AND DUST

CONSOLIDATED ZINC PTY. LTD.

FOURTH REPORT

"RECOVERY OF ZINC AND CADMIUM"

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1. SUMMARY

The use of sodium sulphate solution for the elution of cadmium and zinc from Zeocarb 225 resin has been demonstrated using a 3-split recycle technique. The following operating conditions were used for the test run:

Sodium sulphate concentration:	1.7N
Eluent flowrate:	1.5 gallons/sq.ft./minute
Volume of first split:	2 bed volumes
Volume of second split:	2.5 bed volumes
Volume of third split:	2 bed volumes

The volume of eluent used is the maximum allowed by other process considerations.

The results of the elution were quite satisfactory. After 8 cycles, approximately 2.2 per cent. of the cadmium was reporting in the third split. For equilibrium conditions this figure would increase slightly but the conditions appear quite adequate. There is probably scope for more economic operation by reducing either the quantity or concentration of the eluent.

Under the conditions of the test, the lead was completely eluted but if higher concentrations are encountered in practice there could be a poisoning effect.

On the industrial scale, an elution cycle operated at the same conditions as the test cycle would take 183 minutes to complete.

2. INTRODUCTION

The second report in this series on the recovery of zinc and cadmium from smelter fume and dust described the use of sodium sulphate as the ion exchange eluent. The characteristics of the elution of zinc and cadmium were examined at three sodium sulphate concentrations. The investigation showed that sodium sulphate was a satisfactory eluent but because of its relatively low solubility at low temperatures, provision would need to be made for some heating of the solutions to maintain sufficient solubility during winter months.

The work covered by the second report did not include any investigation of the recycle technique which would be necessary for the lowest cost operation. This fourth report has therefore described this aspect of sodium sulphate elution for a set of conditions calculated to give complete elution.

In determining the conditions for the elution test, it was necessary to observe two limiting factors. Firstly the total volume of eluent per day on the industrial scale is limited to approximately 6000 gallons and secondly the duration of the elution cycle must be short enough to allow for six elutions per day with reasonable stand-by time.

3. MATERIAL EXAMINED

The ion exchange work was based on a synthetic pregnant liquor made up from cadmium metal, zinc sulphate and lead oxide.

4. EXPERIMENTAL

4.1 Ancillary Materials

Resin: Zeocarb 225 resin was used. The material was portion of a 0.5 cu.ft. sample of the usual commercial grade supplied by the Permutit Co. Ltd.

Sodium sulphate: Sodium sulphate from a sample supplied by Courtaulds (Aust) Pty. Ltd. was used. Further details of this sample were given in the Second Report (page 2).

4.2 Equipment and Operating Procedure

The ion exchange equipment was as described in section 2.2.5 of the second report.

Synthetic pregnant liquor was made up from cadmium metal dissolved in sulphuric acid, and zinc sulphate dissolved in water. A small lead and chloride concentration was supplied by dissolving lead oxide in hydrochloric acid and adding it to the zinc-cadmium solution. The pH of the solution was adjusted to 1.4 with precipitated zinc hydroxide.

Nine adsorption-elution cycles were carried out using the two-column set. The adsorption cycle started with a freshly eluted column connected as the trailing column to the other column already partly loaded. Two-column adsorption was continued until the leading column broke through. The loaded column was then eluted while the adsorption continued with the remaining column. At the end of the elution, the eluted column was brought on line to commence a new adsorption cycle.

The pregnant liquor flow during adsorption was 220 ml per minute (2.1 gallons per sq. ft. per minute). This flow was increased from the 200 ml per minute in the previous investigation so that two cycles could be completed in one day.

The elution was carried out in seven stages according to the following procedure:

Stage 1 At break-through the adsorption was stopped and the liquor in the leading column was displaced through the trailing column with water. The displacement flow rate was 220 ml per minute for seven minutes. At the completion of stage 1 the adsorption was resumed.

Stage 2 The column was backwashed at 400 ml per minute (3.8 gallon per sq. ft. per minute) until 6000 ml were collected. The backwash was rejected.

Stage 3 The backwash liquor in the column was displaced with No.1 recycle liquor at 140 ml per minute until 1400 ml (one voids volume) had been collected.

Stage 4 The flow of No.1 recycle liquor was continued at 160 ml per minute (1.5 gallons per sq. ft. per minute) until 6000 ml of eluate were collected. This liquor was then the high-grade split of the elution.

Stage 5 The elution was continued at the same flowrate using No.2 recycle liquor until a further 7400 ml were collected. This split was then the No.1 recycle liquor for the next elution.

Stage 6 The elution was continued at the same flowrate using fresh eluent solution until 6000 ml were collected.

Stage 7 The eluent in the column was displaced with water at 160 ml per minute. The displacement was continued until 1400 ml were collected. The liquors from stages 6 and 7 were combined to make the No.2 recycle for the next elution.

5. RESULTS

Continuous adsorption and elution was carried out for a total of 9 cycles. The analyses of the liquors used for adsorption and elution are shown in Table 1.

Table 1

Liquor Analyses
(grams/litre)

Pregnant Liquor	
Cadmium	2.87
Zinc	1.00
Lead	0.003
Chloride	1.29
Sulphur Dioxide	6.69
pH	1.4
Sodium Sulphate Eluent	
First seven elutions	
Sulphate	81.6 (1.70N)
Elutions 8 & 9	
Sulphate	85.4 (1.80N)

The pregnant liquor break-through volumes are shown in Table 2.

Table 2

Break-through volumes

Cycle No	Volume (Litres)
1	49
2	52
3	51
4	51
5	57
6	55
7	52
8	56
Average	53

The average break-through volume was 53 litres, equivalent to a cadmium loading of 153 grams (3.2 lb/cu.ft.) and a zinc loading of 53 grams (1.1 lb/cu.ft.).

Samples were assayed from elutions 2, 4, 6 and 8. The results are shown in Table 3. Table 4 shows the calculated cadmium content of the various stages. The results show that the elution system was approaching equilibrium although it had not been reached after 8 cycles. The average break-through volume was 53 litres and therefore at equilibrium, there should be approximately 150 grams of cadmium in the stage 4 eluate. The final figures indicate approximately 140 grams of cadmium in stage 4 and therefore the concentration of the recycle stages must still be increasing and could be expected to increase a further 10 per cent.

If it is assumed that the results of elution 8 do represent the equilibrium conditions then the proportion of cadmium actually eluted in each fraction is as shown in Table 5.

Table 3

Eluate Assays
(grams of metal/litre)

Elution Number	2	4	6	8
Stage 4				
Cadmium	21.0	22.2	24.3	23.0
Zinc	9.65	9.4		
Lead	0.03	0.027		
Stage 5				
Cadmium	2.43	3.08	3.54	3.84
Stage (6 & 7)				
Cadmium	0.19	0.32	0.42	0.40

Table 4

Cadmium Content of Eluate
(grams)

Elution Number	2	4	6	8
Stage 4	126	133.2	145.8	138.0
" 5	17.0	22.8	26.2	28.4
" (6 & 7)	1.4	2.4	3.1	3.0

Table 5

Elution of Cadmium

Stage	Equilibrium Concentration g. Cd/l	Cadmium Content g.	Cadmium Eluted	
			g	%
4	23.0	138	109.6	79.4
5	3.84	28.4	25.4	18.4
6 & 7	0.40	3.0	3.0	2.2
Totals		169.4	138.0	100.0

The possibility of "royal" barrens was checked by assaying the first 4 litres of barren liquor collected after elution 2 and 4. The cadmium assays were 0.006 and 0.013 g/l respectively. The assays of the bulk barrens collected after these elutions are shown in Table 6. The results indicate an absence of significant "royal" barrens.

Table 6

Bulk Barren Assays
(grams of metal/litre)

After Elution No.	2	4
Cadmium	0.00076	0.0019
Zinc	0.009	0.0015
Lead	0.0001	0.00035

The lead adsorbed on the resin from the pregnant liquor balances (within the accuracy of the test) the lead present in the high-grade eluate. Assays of the resin for lead before and after the tests showed no increase in the lead content and there was no evidence of sulphur dioxide affecting the resin.

6. DISCUSSION

The experimental work has demonstrated a satisfactory set of elution conditions. In the eighth elution only 2.2 per cent. of the cadmium appeared in the final split and therefore the elution of cadmium would virtually be complete.

It is considered that the process would be satisfactory if up to 5 per cent. of the cadmium appeared in this final fraction.

Therefore either the concentration or quantity of the eluent could be reduced slightly for more economic operation. It is difficult to estimate the optimum conditions from this work but in view of the fact that the maximum allowable quantity of eluate was produced in the testing, it is unlikely that the sodium sulphate concentration of the eluent could be as low as 1.3N as predicted in the Second Report.

The zinc and cadmium loadings of the resin were 1.1 and 3.2 lb/cu.ft. respectively. These are significantly greater than the figures reported in the first report when actual leach liquors were used. It is probable that the difference between synthetic and actual pregnant liquors is very important in the adsorption cycle and, in particular, the question of lead adsorption and elution by sodium sulphate should be examined more thoroughly.

In the experimental work all the lead in the pregnant liquor was absorbed and eluted but the lead concentration was so low that it may not have been typical. If the lead concentration of the pregnant liquor is appreciable one can visualise a poisoning effect by the precipitation of lead sulphate in the resin during sulphate elution.

Table 7 shows the elution cycle timing for the industrial scale using the same cycle as used in the experimental testing, i.e. a 3-split elution with 2 bed volumes in the high-grade fraction and a flowrate of 1.5 gallons per sq. ft. per minute.

Table 7

Elution Cycle Timing - Industrial Scale

Stage No.	Operation	Bed Volumes	Rate g.p.m.	Time Mins.
1	Forward Displacement	0.5	24	10
2	Backwash	1.5	45	17
3	Displacement with No.1 Recycle	0.5	24	10
4	Elution	2.0	24	42
5	Elution with No.2 Recycle	2.5	24	52
6	Elution with fresh eluent	2.0	24	42
7	Displacement	0.5	24	10
Total time				183

The total time is 183 minutes and for an anticipated six elutions per day, there would be approximately 18.5 hours of operation and 5.5 hours available stand-by time.

7. RECOMMENDATIONS

It is recommended that the industrial operations of the ion exchange plant be commenced with elution conditions similar to this test work and that optimum conditions for the elution be determined on the industrial scale when the characteristics of the adsorption cycle will be accurately known.

The question of adsorption and elution of lead should be given further investigation.