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## **RECOVERY OF ZINC AND RARE EARTHS FROM ABU RUSHIED FERRUGINOUS ORE MATERIAL, SOUTH EASTERN DESERT, EGYPT**

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### **Abstract**

This paper is concerned with the recovery of separate Zn and REEs pure concentrates from a sulphate leach liquor of Abu Rushied ferruginous ore material. Preparation of separate Zn/REEs concentrates was carried out by either selective oxalate precipitation of the REEs or else by bulk hydroxides precipitation followed by re-dissolution of Zn as zincate. The leached REE values could also be recovered in two main steps namely; precipitation of LREEs as their double sulphate during or directly after the acid leaching while the potentiality of individual separation of the HREEs concentrate left behind was studied through the displacement technique using the cationic exchange resin Dowex 50W-X8. A tentative flowsheet for the overall treatment of Abu Rushied ore material is also presented.

### **Introduction**

Abu Rushied mineralization is mainly associated with basic lamprophyre dykes intruded in some shear zones that are cutting through cataclastic quartzo-feldspathic rocks (gneisses and granites). The area has actually been subjected to several alteration and mineralization processes (Ibrahim et al., 2002 and 2004<sup>(1-2)</sup>). The latter is mainly manifested in REEs, Zn, U and Sn at the shear zone and by Th, Nb, Ta, Zn, Ga and U in the cataclastic rocks. On the wall zone of some dykes, Zn, REEs besides U, V and Cu could be found adsorbed on clay and iron oxide minerals. According to Rashed (2005)<sup>(3)</sup>, several minerals of these metal values have actually been identified.

In the light of the one of the several occurrences of potential economic importance of Abu Rushied area as a poly-mineralized prospect, a technological sample of Abu Rushied mineralized ore material was collected. In a previous work the nature of these sample as well as its leaching characteristics have been properly studied by the present authors<sup>(4)</sup>. In these studies, it was ascertained that the technological sample assays 5%Zn and 3.1%  $\Sigma$ REEs and that these metal values are intimately associated with the iron oxide mineral goethite. The studied leaching characteristics have indicated that the optimum leaching factors involved 200g/l

H<sub>2</sub>SO<sub>4</sub> in a solid/liquid ratio of ½ for 6 hrs at 100 °C and in the presence of 20% of ore weight of NaClO<sub>3</sub>. The latter besides creating the powerful oxidizing chloric acid would provide adequate Na<sub>2</sub>SO<sub>4</sub> to precipitate the LREEs as their double sulphates. The present paper is thus involved in studying the possible different methods for the separation of Zn and RE pure concentrates from the obtained sulphate leach liquor.

## **Experimental**

### *Recovery Procedures*

#### *Precipitation procedures*

For the recovery of Zn and REEs, a proper sulphate leach liquor containing 16.3 g/l Zn, 11.5 g/l REEs and 54.15 g/l Fe<sub>2</sub>O<sub>3</sub> was prepared. From the latter, two main precipitation procedures have been performed after a prior iron separation at pH 3.5. These include selective oxalate precipitation of the REEs at different pH values as well as bulk hydroxides precipitation of both Zn and REEs at pH 7-8.

#### *Ion- exchange procedure for individual REEs separation*

For individual REEs separation, the band displacement technique using proper elution by EDTA solution of REEs- saturated resin bed through another resin bed in the Cu (II) form has been used. For this purpose, a pure HREO concentrate was first prepared through bulk hydroxide precipitation followed by alkali re-dissolution of Zn as its zincate. Calcination of the HRE hydroxides left behind was then subjected to purification by NH<sub>4</sub>Cl solution followed by its dissolution in HCl and adjusting the pH to 2.5. The pH of the EDTA eluant (0.015M) was adjusted to pH 8.5 by NH<sub>4</sub>OH. The eluted REEs fractions were periodically collected after complete Cu elution for analysis of the separated individual REE and Y. In this procedure, a contact time of 20 min. was used.

## **Results and Discussion**

### *Results of Zinc and REEs Recovery*

As mentioned above, to main alternatives for the separate recovery of Zn and REEs have been found most convenient; namely:

- a- Selective oxalate precipitation of the REEs by proper adjustment of pH to ensure non precipitation of Zn.
- b-Bulk or co-precipitation of Zn and REEs as their hydroxides followed by selective re-dissolution of Zn as zincate using excess base.

*Selective precipitation of REEs oxalates*

According to Habashi (1993)<sup>(5)</sup>, the REEs form actually insoluble oxalates and can thus be used for their separation. However, Zn is among several other metals which could also form insoluble oxalates and therefore recovery of the REEs as their oxalates should be performed under specific conditions particularly the pH.

Two oxalate precipitation tests at pH 3 and 4.5 have been performed, however, after a prior precipitation of Fe and Al as hydroxides at pH 4.5. The filtered and washed solution assaying 11.3 g/l Zn and 8.02 g/l REEs was divided into 2 samples:

- (a) In the first test, the pH of 4.5 was kept and 10% oxalic acid was added.
- (b) In the second test, the pH of the filtrate was first decreased to pH 3 before adding the oxalic acid. The precipitated oxalates were properly filtered, washed and dried before being subjected to ESEM analysis (Table 1).

From the obtained results, it is clearly evident that precipitation at pH 3 has actually resulted in the co-precipitation of both Zn and REEs oxalates. In the latter, Zn amounted to 41.1% while Y attained 25.87% and the heavy REEs Ho, Er and Yb assayed 7.48, 3.80 and 1.34% respectively. On the other hand, oxalate precipitation at the higher pH value of 4.5 was relatively greatly successful where Zn assayed only 1.08%. In the meantime, Y amounted up to 53.76% while Ho attained 16.23% whereas Er has attained up to 6%. This result indicates that pH control of precipitation is quite important in obtaining selective precipitation of either Zn or RE oxalates.

**Table (1): ESEM analysis of REE/Zn oxalates precipitated from Abu Rushied sulfate liquor at pH3.0 and 4.5 (Average of 6 spots)**

REE / Zn	(Wt %)	
	pH 3.0	pH 4.5
Zn	41.10	1.08
Y	25.87	53.76
Ho	7.48	16.23
Er	3.80	5.99
Yb	1.34	1.00
La	0.51	0.78
Ce	0.22	0.40
Pr	0.19	0.48
Nd	0.37	0.87
Sm	0.46	0.54

*Co-precipitation of Zn and REEs hydroxides*

According to Habashi (op. cited), both  $Zn^{2+}$  and  $REE^{3+}$  can be precipitated as their respective hydroxides at pH 7 for Zn and in the range from 6.8 (Y) to 8.4 (La) while for Ce IV, it would be precipitated quite early at pH 2.7. Accordingly, it would be possible to co-precipitate Zn and RE hydroxides by pH control. The precipitated Zn and RE hydroxides can then be treated with a concentrated alkali base to dissolve Zn as zincate (Cotton and Wilkinson, 1976) <sup>(6)</sup> while the RE hydroxides would be left behind. It is interesting to mention herein that, Ce assay is quite low in the working ore material; a matter which favors the prior precipitation of  $Fe^{3+}$  and Al at pH 4.5.

A proper amount of the prepared leach liquor was firstly subjected to ferric iron precipitation by increasing its pH to 4.5 by 20% NaOH solution. The obtained filtrate and washings of the Fe/Al cake was then neutralized to a pH of about 8 by 20% NaOH solution where both Zn and REEs were precipitated as their respective hydroxides.

From the ESEM analysis of 4 spots of this precipitate, its average composition was calculated and given in table (2). From this table, it is clear that Zn assay up to ~16% while HREEs (Ho, Er, Yb and Y) assay about 12% and the LREEs (La, Ce, Pr, Nd and Sm) are less than 2%. These figures thus indicate almost complete precipitation of Zn and the HREEs metal values. The low assay of the LREEs which represent about 65 % of the total input REEs is most probably due to their prior precipitation as their double sulfates. On the contrary, Y and the heavy rare earth sulfates are quite soluble and remain in solution until their hydrolytic precipitation at a pH value of about 7-8.

*Zn/REEs separation*

Trials to separate Zn by increasing the pH of iron-cake filtrate up to 12 at room temperature in a manner to keep Zn in a soluble state (zincate) while the REE would be selectively precipitated as their hydroxides. However, it was found that this procedure is inefficient for dissolving Zn as the soluble zincate after its co-precipitation with the REE i.e. most of Zn has actually remained as precipitated hydroxide together with the REE hydroxides. This is most probably due to the weak concentration of NaOH beside temperature that are required for re-dissolving Zn. In fact, Zn can selectively dissolve from combined REE/Zn hydroxides by using strong NaOH concentration at high temperature.

**Table (2): ESEM average analysis of Zn and REE precipitate at pH 8 of Abu- Rusheid sulfate leach liquor**

Element	wt %				
	Spot(1)	Spot(2)	Spot(3)	Spot(4)	Average
Zn	14.71	13.56	21.93	13.20	15.85
Y	9.72	9.40	9.79	7.20	9.03
Yb	2.36	1.73	1.95	1.96	2.00
Er	1.12	0.85	1.05	1.06	1.02
Ho	0.33	0.26	0.57	0.36	0.38
La	0.33	0.39	0.64	0.34	0.43
Ce	0.47	0.46	0.55	0.23	0.43
Pr	0.46	0.22	0.42	0.00	0.37
Nd	0.16	0.42	0.36	0.00	0.31
Sm	0.58	0.23	0.34	0.25	0.35

Accordingly, the obtained bulk Zn /REEs hydroxide precipitate was subjected to two dissolution tests. Using 40% NaOH in a solid-liquid ratio of 1/5 at 100°C for 2hr, the analyzed RE hydroxides left behind after filtration indicated about 7% Zn and about 32% total HREE. Using 40% NaOH solution at a S/L ratio of 1/100 at 100°C for 4hr resulted in a RE hydroxide residue assaying only 0.6% Zn and up to about 64% total HREE (Table3).

#### *Potentiality of Individual REEs Separation*

In the present work, it was found advantageous to individually separate the REEs from the prepared REO concentrate. For this purpose, the displacement chromatography technique<sup>(7-9)</sup> via Dowex 50W-X8 cation exchange resin has been used.

Individual separation of REEs by the displacement chromatography technique involves indeed two steps:

- 1- Loading or adsorption of pure mixed REEs upon a resin bed in the H-form using a loading column.
- 2- Normal elution by EDTA followed by displacement elution (displacement chromatography) through a second resin bed in the Cu-form (retaining column) where the eluted Ln EDTA would progressively displace Cu II according to the stability constant of each REE with the chelating EDTA complex (Table 4).

**Table (3): ESEM average analysis of the REEs' residue after Zn selective leaching of their combined hydroxides precipitate**

Element	wt %			
	Spot(1)	Spot(2)	Spot(3)	Average
Zn	0.59	0.69	0.55	0.61
Y	47.93	43.211	34.11	41.75
Yb	16.50	14.13	11.60	14.08
Er	8.61	6.70	5.59	6.97
Ho	2.91	2.03	1.46	2.13
La	0.55	0.43	0.60	0.53
Ce	0.00	0.15	0.20	0.18
Pr	0.15	0.19	0.00	0.17
Nd	0.91	0.72	0.27	0.63
Sm	0.79	0.00	0.17	0.48

**Table (4): Stability constants for rare earth-EDTA and-HEDTA chelates(after Powell,1988)**

Rare earth	EDTA *	HEDTA **
Y <sup>+3</sup>	18.09	14.65
La <sup>+3</sup>	15.50	13.46
Ce <sup>+3</sup>	15.98	14.11
Pr <sup>+3</sup>	16.40	14.61
Nd <sup>+3</sup>	16.61	14.86
Sm <sup>+3</sup>	17.14	15.28
Eu <sup>+3</sup>	17.35	15.35
Gd <sup>+3</sup>	17.37	15.22
Tb <sup>+3</sup>	17.93	15.32
Dy <sup>+3</sup>	18.30	15.30
Ho <sup>+3</sup>	-	15.32
Er <sup>+3</sup>	18.85	15.42
Tm <sup>+3</sup>	19.32	15.59
Yb <sup>+3</sup>	19.51	15.88
Lu <sup>+3</sup>	19.83	15.88

\* at 20° C    \*\* at 2° C

The process can actually be represented by the following equations where  $R^-$  denotes the fixed ion exchange sites of the resin; viz

In loading:



In normal elution:



In displacement elution:



For the preparation of a pure mixed REO sample, a part of sulfate leach liquor was first subjected to alkali precipitation of most iron and alumina at pH 4.5 while the pH of the filtrate was raised to 9 to precipitate the Zn and REEs hydroxides. To purify the latter from Zn, it was subjected to a fairly strong solution of  $NH_4Cl$  while the remaining residue was re-dissolved in 1:1 HCl followed by re-precipitation at pH 5.2 to remove any remaining Fe and/or alumina. After filtration the REEs were precipitated using oxalic acid followed by ignition at 900 °C to obtain REO concentrate. Composition of the latter was calculated and found to contain about 95% total REO distributed in wt% as given in table (5).

**Table(5): Composition of the prepared REO concentrate from the pregnant sulfate leach liquor of the working Abu-Rushied ore material**

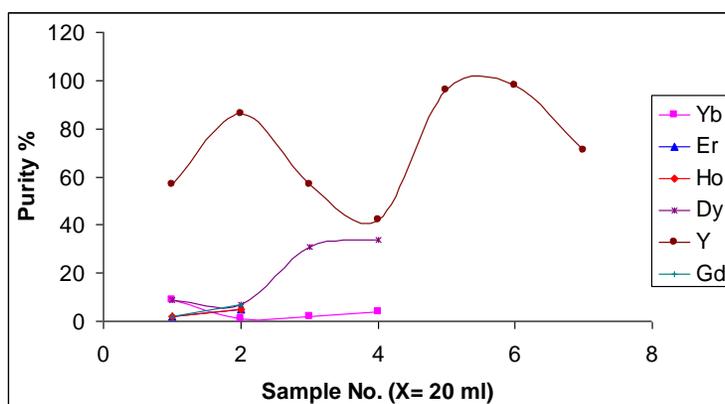
REO	Wt %
$Y_2O_3$	72.5
$Dy_2O_3$	9.8
$Yb_2O_3$	4.0
$Er_2O_3$	2.5
$Ho_2O_3$	0.8
$Gd_2O_3$	0.6
$Sm_2O_3$	0.4
$Nd_2O_3$	1.2
$La_2O_3$	1.3

About 0.2 g of the prepared pure REO concentrate was dissolved in the minimum amount of concentrated HCl and was then completed to 50 gram after pH adjustment to 2.5 by ammonia solution. A small loading column (0.55 cm internal diameter) was packed with 3 ml of the working solid of 100-200 mesh size (Dowex 50W -X8) in its  $H^+$  form and the prepared  $RECl_3$  solution was passed through it. The loaded REEs resin bed was then eluted by the prepared EDTA solution of 0.015 M adjusted at pH 8.5 by  $NH_4OH$ , through a second retaining column (0.55 cm

internal diameter) packed with about 10ml of the same resin but in the  $\text{Cu}^{\text{II}}$  form. A contact time of 20 min. was used and the eluted samples were periodically collected every 20 ml. The latter were subjected to oxalate precipitation of its REE content followed by calcination at  $900^{\circ}\text{C}$ . The obtained REO sample fractions were then analyzed by ESEM and the obtained results are summarized in table (6) and schematically shown in Fig.(1).

**Table (6): ESEM analysis of EDTA elutate fractions of Abu Rusheid REO concentrate through Dowex 50W-X8 resin bed in the copper<sup>II</sup> state**

Fraction No. X = 20 ml	Total vol., ml	RE <sub>2</sub> O <sub>3</sub> wt., g	Individual RE <sub>2</sub> O <sub>3</sub> Distribution %										
			Yb	Er	Ho	Dy	Y	Gd	Eu	Sm	Nd		
Cu <sup>II</sup> Elution	520	-											
1	540	0.0293	7	9		9	57						
2	560	0.0285	1	1		7	86						
3	580	0.0267	4	2	2	31	57	2					
4	600	0.0261	9	4	5	34	42						
5	620	0.0253	3				96						
6	640	0.0234	1				98						
	650	0.0125	3				71	7	2	5	8		
Total	wt.	0.1718											



**Fig. (1): Elution curves obtained for Abu Rusheid REEs mixture with 0.015 M EDTA**

From the obtained results, it has been found that an eluant volume of 520 ml was passed for complete  $\text{Cu}^{\text{II}}$  elution before Ln breakthrough. In addition, it is clearly evident that separation to high purity individual REEs is difficult in one run. This is

mainly due to the composition of the input concentrate where Y attains a concentration of up to 72.5% while the other 3 associated HREEs are relatively minor. In the meantime and according to table (6), Y would be eluted between Dy and Tb, however, due to the small difference between the stability constants of Dy and Y, their separation would be difficult. This is actually demonstrated in their combined elution in samples No. 1 to 4 and in which Dy varies between 7 and 34% and Y varies between 42 and 86%. After sample No. 4, Dy elution was ended and Y assay increased in samples No. 5 and 6 up to 96 and 98% respectively. It has to be mentioned herein that Dy-Y separation would be better achieved by HEDTA due to the reasonable difference of their stability constants with this chelate (15.30 and 14.65 respectively). On the other hand, the very small concentrations of Yb, Er and Ho in the input REO concentrate sample might have been better separated by using a longer contact time and/or a longer retaining resin bed. Similarly, the very small amounts of Gd, Eu, Sm and Nd in the input sample have been shown in the last eluate sample No. 7 as expected, however with 71% Y.

Finally, it might be interesting to mention that Y percent recovery in samples 5 and 6 of purity 96 and 98% attain more than 38% of input Y content. On the other hand, the relatively high percent of Dy in eluate samples No. 3 and 4 could be improved through a 2<sup>nd</sup> run of such samples in which better working conditions must be applied.

#### *Proposed Technical Flowsheet*

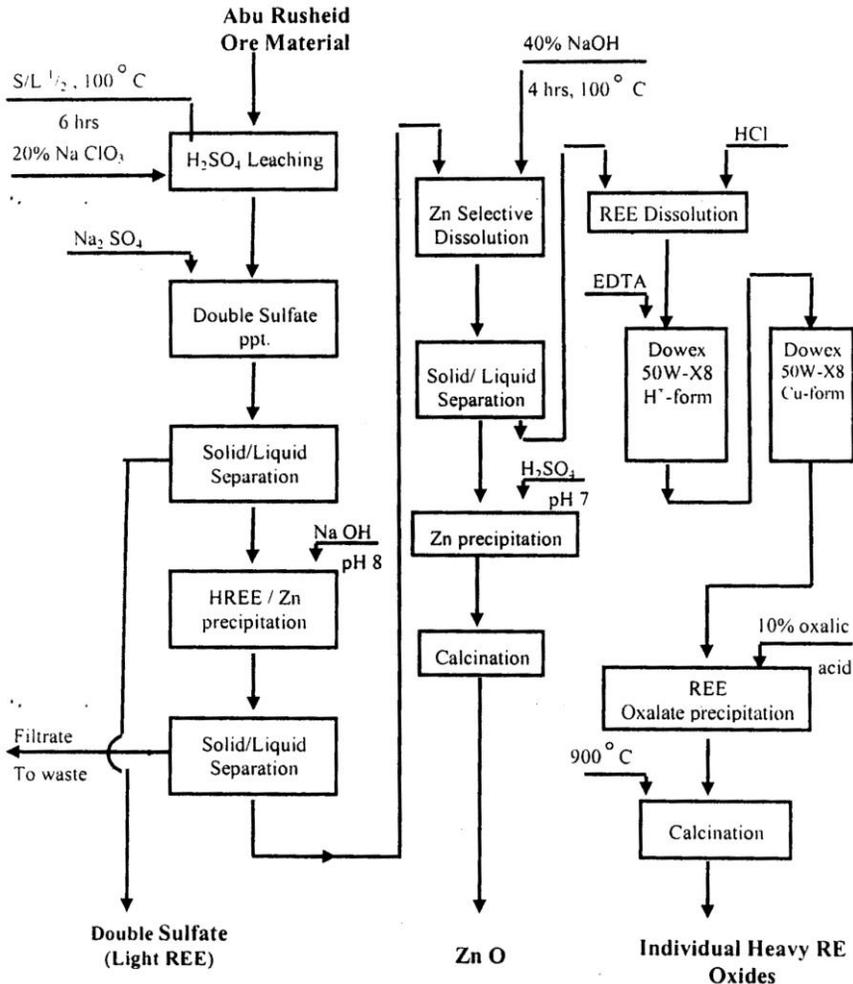
From the obtained data of processing Abu Rusheid ore material, a tentative flowsheet for treating such material has been proposed for the recovery of REEs and Zn. In this flowsheet (Fig.2), the obtained sulphate leach liquor would first be subjected to the precipitation of the double sulphates of the LREE by ensuring adequate presence of Na<sub>2</sub>SO<sub>4</sub>. The Zn/HREEs in the filtrate would be then subjected to bulk hydroxides precipitation to be later separated by selective dissolution of Zn in an excess base (40% NaOH, S/L=1/100, 4hrs at 100 °C). After filtration, the filtered was re-acidified to precipitate Zn as its hydroxides followed by its calcination to ZnO. The RE hydroxide left behind was then purified and dissolved in HCl to individually separate its content of the HREEs.

#### **Conclusions**

Preparation of separate Zn / REEs concentrates from Abu Rushied sulphate leach liquor was successfully carried out by their bulk hydroxides precipitation to be later

separated by selective dissolution of Zn in an excess base. However, a prior Fe/Al separation was found necessary in order not to contaminate the prepared Zn or REEs concentrate.

The present REEs values could successfully be achieved in two main steps; namely precipitation of the LREEs as their double sulfates during or directly after the acid leaching while the individual separation of the HREEs concentrate would be carried out through the displacement technique using a proper cation exchange resin. Close adjustment of the working conditions are quite necessary to achieve acceptable purity.



**Fig. (2): Proposed technical flowsheet for treating Abu Rushied ore material.***Acknowledgments*

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