# A PROCESSING TECHNOLOGY FOR HEAVILY WEATHERED RARE EARTH ORES OF DONG PAO / VIETNAM

8. Merker (Lecturer), Rohstoff Consulting Dresden GmbH

G. Schulz and Ch. Cichos, Forschungsinstitut für Aufbereitung Freiberg (FIA)

H. Richter, Stickstoffwerke Piesteritz AG

#### SUMMARY

The bastnaesite deposit of Dong Pao is situated in the outermost north of Vietnam within the Lai Chau district. Due to a heavy weathering and the association of bastnaesite with large amounts of fluorite and baryte the ores are difficult-to-treat.

On the basis of laboratory and pilot scale tests a technology comprising a washing and classifying operation as initial and vital processing stage was developed. The washing fines contain some 30 % RE-oxides with a RE-recovery of 63 %. Because of the specific properties of this low grade bastnaesite concentrate a new metallurgical process permitting its industrial utilization had to be developed. This process features the leaching of the concentrate by sulphuric acid virtually practicable in solid state by means of rotary drums with 200 up to 300 °C only.

Additional stages of the processing technique are a baryte flotation to obtain drilling grade baryte and a high intensity magnetic separation yielding a second bastnaesite concentrate of about 38 % RE-oxides. Both the two bastnaesite concentrates can be mixed for metallurgical treatment.

#### INTRODUCTION

Bastnaesite is a mineral containing about 64 % Rare Earth metals (RE). According to Falconnet [1] about one third of the world RE production based on bastnaesite concentrates in 1987.

Main producer of bastnaesite are the deposits of Mountain Pass/USA and Bayan Obo/China. The separation of bastnaesite from associated minerals like baryte, calcite, fluorite, quartz, celestite and haematite is carried out above all by flotation processes [2,3,4,5]. The hydrometallurgical production of REmetals and RE-compounds from bastnaesite normally bases on concentrates containing 60-70 % RE-oxides.

Several comparatively small and unknown bastnaesitic RE deposits are situated in the north Vietnam district Lai Chau. The RE-oxide-content of the ores of the main ore body ranges from 5 up to 14 %. Bastnaesite is mainly associated with baryte and fluorite. Characteristic of the deposit are a deep weathering and heavy decomposition making the ores difficult-to-treat. The

investigations into the beneficiation of the Dong Pao ores were carried out on laboratory up to pilot scale during exploration activities from 1985 to 1989. Thereby the aim was the development of a practicable processing technique permitting both the production of useful bastnaesite concentrates and baryte for drilling mud.

#### ORE CHARACTERISTIC

Main constituents of the ores according to the decreasing order of frequency are baryte, fluorite, bastnaesite, quartz, Feand Mn-hydroxides.

Table 1. Particle size distribution, assay and distribution of RE, baryte and fluorite of a composite sample of the Dong Pao ore according to [9]

Size range	Distri	bution	%		Assay	%	
mm	mass	RE <sub>2</sub> 0 <sub>3</sub>	baryte	fluorite	$RE_2O_3$	baryte	fluorite
< 0.015	16.8	43.9	7.5	4.1	35.7	22.3	3.9
0.015-0.032	7.4	8.0	7.3	5.1	14.7	48.8	11.2
0.032-0.063	5.7	5.4	5.3	4.3	12.5	48.6	12.7
0.063-0.1	9.1	9.7	10.2	7.3	13.9	58.3	13.4
0.1 -0.315	11.1	10.9	11.4	10.9	12.9	53.4	16.5
0.315-0.5	6.5	6.0	6.5	8.4	12.1	51.7	21.6
0.5 -1.0	12.2	7.7	12.2	17.4	8.3	51.9	23.9
1.0 -2.0	12.4	4.8	14.8	18.0	5.1	62.0	24.4
> 2.0	18.8	3.6	24.8	24.5	2.6	68.1	21.8
	100.0	100.0	100.0	100.0	13.1	51.9	16.8

From the aspects of ore dressing two properties of the ores are especially important. Caused by the weathering there is firstly the primary slime proportion associated with a distinctly grain-size-dependent distribution of the useful components. Secondly the bastnaesite is associated with fluorite. Having similar flotation properties the separation of this two minerals from each other is relatively complicated. It is worth mentioning that on that subject several articles have been published above all by chinese researchers in recent years [3,5,6,7,8].

Both the slime proportion and the association with fluorite have precluded the separation of normally marketable bastnaesite concentrates so far.

The characteristic distribution of useful components mentioned has led to a considerable enrichment of bastnaesite in the fines. As can be seen in Table 1 the RE-content increases up to 35 % RE-oxides below 15 microns. Thereby this fraction contains more than 40 % of the RE.

The required task was the harnessing of the bastnaesite fines. By developing both a combined technique consisting of the stages washing, flotation, magnetic separation and a special metallurgical treatment of the bastnaesite concentrates the problems could be solved.

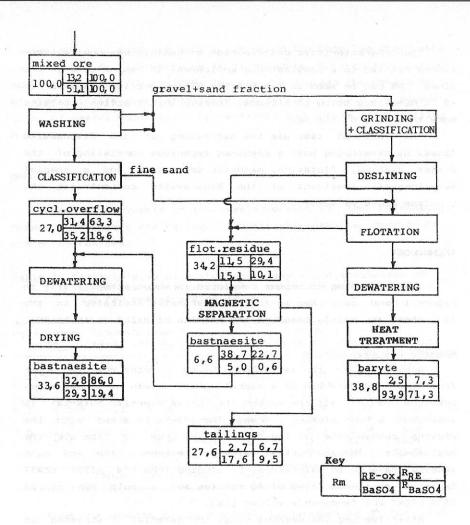
#### TECHNOLOGY

The processing technique developed is shown schematically in Figure 1 and described as follows. Parameter indicated in the flow sheet are mainly based on the results of pilot scale tests.

# Washing and classifying

According to the technology the run-of-mine ore is drawn from the crude ore bin to a vibrating wet screen of 40 mm sieve aperture. Having left the screen the coarse oversize material is undergone a hand picking process. The undersize mixed with the picking concentrate is led to a washing drum to liberate the bastnaesite. Thereby certain values of residence time and pulp density have to be maintained. Concluding from the pilot scale tests a residence time of 40 minutes and a pulp density of 1550 g/cm<sup>3</sup> are favourable values [12].

After leaving the washing stage the material is screened at 2.5 mm cut-size by means of a rotary screen. The fraction below 2.5 mm is delivered to a classifying circuit consisting of an upstream classifier and a spiral classifier. Via a surge bin the overflow of the upstream classifier flows subsequently to a hydrocyclone arrangement. Simultaneously the classifier underflow flows to the spiral classifier separating the remaining fines as a scavenging stage. As additional rinsing-water the spiral classifier overflow is circulated to the rotating screen.



<u>Fig. 1.</u> Simplified processing flow sheet for the Dong Pao Rare Earth ore

Aiming at maximum recovery of the fine fractions in the mentioned hydrocyclone stage the hydrocyclones are connected in a special manner as to be seen in Figure 2.

At a cut size of 0.015 mm the overflow of the first two hydrocyclone stages yields the valuable product.

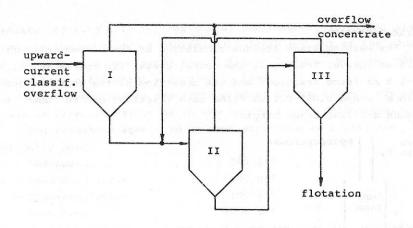


Fig. 2. Flow sheet of the hydrocyclone stage according to [12]

Adding a flocculant to the overflow product prior to being pumped to the thickener has proved beneficial. The thickener slurry is dewatered subsequently by filter presses down to about 25 % residual moisture. The thickener overflow water and the water from the filter presses can be used as recycling water.

The specific water consumption of the total washing stage without any recycling of water is designed to be about 19  $\rm m^3/t$  [17].

For the drying of the filter cake a rotary dryer can be used. The filter cake has proved to show favourable drying properties. While passing the rotary dryer the cake pieces are formed to ball-shaped agglomerates with only 5 % fines below 0.04 mm grain size [13].

The dried product contains about 31 % RE-oxides. The RE-recovery attains 63 %.

In addition to bastnaesite (42 %) the first bastnaesite concentrate contains above all baryte (about 35 %) and fluorite (about 8 %). Furthermore there are concentrated the Mn- and Feoxides of the ore causing a brown colour. The composition of the first bastnaesite concentrate is shown more detailed in Table 2.

### Baryte flotation

The washing stage residue consisting of the screen oversize > 2.5 mm (gravel fraction), the spiral classifier coarse fraction 0.1-2.5 mm (sand fraction) and the underflow of the third hydrocyclone stage 0.015-0.1 mm (fine sand fraction) can be used to produce drilling grade baryte.

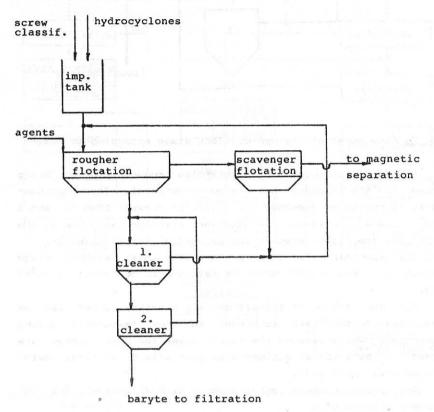


Fig. 3. Flow sheet of the flotation stage according to [14]

Thereby prior to flotation the gravel and the sand fractions are mixed and fed to a grinding circuit consisting of a spiral classifier and a ball mill grinding the feed material down to below 0.16 mm. Subsequently the overflow of the spiral classifier is deslimed and added to the fine sand fraction of the third hydrocyclone stage. Prior to being fed to the rougher flotation the material is pumped to a surge tank and adjusted to a pulp

density of 1.42 g/l. The residue of the rougher flotation stage flows to the scavenger flotation. The froth product of the rougher flotation is re-cleaned twice. Figure 3 shows the flow sheet of the baryte flotation according to [14].

Being very stable the froth product of the second cleaning stage is directly delivered to the dewatering by filtration.

The flotation agents to be used according to [9,14] are the following ones:

- FAS-paste	500	g/t
- sodium silicate	750	g/t
- ligninsulfonate	100	g/t
- petroleum	1000	g/t.

Sodium silicate and ligninsulfonate are used as depressants for fluorite, bastnaesite, quartz and oxides. FAS-paste is a technical product of the Fettchemie Chemnitz enterprise consisting of a mixing of C10 up to C20 sodium alkyl sulphates. Emulsified with petroleum it is applied for collecting baryte. Thereby it has proved beneficial to adjust the pH-value to about 9-9.5. At lower pH values fluorite and bastnaesite tend to float along with the baryte.

The flotation process described yields a concentrate of about 94 % baryte and bastnaesite and fluorite 3 % each. Having undergone a heat treatment to decompose the adhering flotation agents the baryte concentrate can be used to produce baryte for drilling mud. The flotation recovery of baryte achieves 87 %. Losses of baryte of 11 % are caused above all by the necessary desliming process prior to flotation.

# Magnetic separation

The mixture of flotation tailings and grinding slimes still contains about 15 % bastnaesite. It has proved useful to treat it by high intensity magnetic separation. By a single wet magnetic separation process on a magnetic testing installation with steel ball matrix a concentrate with 38.7 % RE-oxides could be obtained [10]. This product can be mixed with the first bastnaesite concentrate. Due to the additional magnetic separation stage the total RE-recovery can be increased to 86 %.

# Treatment of the bastnaesite concentrates

Table 2 shows the composition of the mixed bastnaesite concentrate.

Table 2. Composition of the mixed bastnaesite concentrate (%)

RE <sub>2</sub> 0 <sub>3</sub>	BaSO <sub>4</sub>	CaF <sub>2</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> 0 <sub>3</sub>	MnO	wU of	Th	Cu	РЬ	Zn	Nb
				6.0							0.07

Large amounts of gangue minerals like that adversely affect the hydrometallurgical treatment with acidic leaching in pulp as initial stage normally.

Treating the concentrates with sulphuric acid the leaching process could observed to run virtually in solid phase due to the specific structure and composition of the mineral aggregates. The dry decomposition process can be carried out at relatively low temperatures of 200 up to 300 °C. Basing on that phenomenon a non-conventional metallurgical process could be developed avoiding the energy intensive leaching agitation stage.

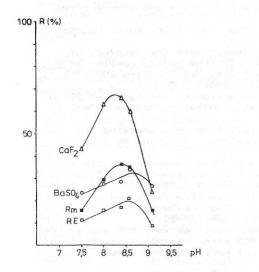
According to [15] the developed process comprises the following steps:

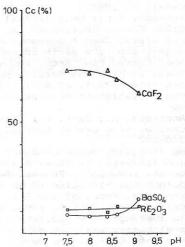
- comminution of the dried bastnaesite concentrate
- mixing with a certain amount of concentrated sulphuric acid (due to the exothermic reaction the mixing turns to virtually dry agglomerates)
- heating of the agglomerates up to 200-300 °C to remove fluorine (This process stage can be carried out favourably by means of rotating drums.)
- dissolving of the formed RE-sulphates and Fe-sulphate with cold water
- removal of the insoluble components (baryte, gypsum, quartz  $\mathrm{MnO}_2)$  by filtration
- precipitation of the RE as Na-RE-double sulphates and filtration
- reaction of the Na-RE-double sulphates with NaOH to form REhydroxides, separation from the Na-sulphate-solution by filtration
- treatment of the filtrates with NaOH, oxidizing agents and soda to remove components like  ${\rm Fe}^{3+}$ ,  ${\rm Mn}^{2+}$ ,  ${\rm Zn}^{2+}$ ,  ${\rm Ca}^{2+}$  and other bivalent metals by precipitation and filtration

- recovering of the sodium sulphate from the filtrates by cooling, crystallization, filtration or centrifugation

## Fluorite flotation

Also laboratory tests to separate fluorite and bastnaesite by flotation were a part of the investigations. A laboratory procedure allowing the direct flotation of fluorite from the tailings product of the baryte flotation could be developed.





<u>Fig. 4.</u> Diagram showing the dependence of fluorite flotation on the pH-value according to [16]

The collector used was a technical product consisting of unsaturated C16-C18 fatty acids. For depressing bastnaesite and gangue minerals sodium silicate, ligninsulphonates and sodium fluorosilicate were used. As can be seen in Figure 4 the flotation response of the used samples showed a distinct dependence on the pH-value. An acceptable separation efficiency could be attained only within a narrow pH-range from pH 8 to pH 8.5 about. By laboratory cycle tests fluorite concentrates of more than 90 % could be obtained.

#### SYMBOLS USED

RE Rare Earths

R<sub>m</sub> Recovery by mass

C<sub>r</sub> Content of concentrate

#### REFERENCES

- [1] Falconnet, P.: Rare Earth metals-problems and perspectives. Metall 43(1989)3
- [2] Johnson, N.L.: DeCo Trefoil. Engn. Notebook, Bull. No M4-B128, Denver 30,(1966)4 pp. 9-16
- [3] Luo Jiake; Chen Xiangyong: Research into the recovery of high-grade rare earth concentrate from Baotou complex iron ore, China. Min. proc. and extract. Met., London 1984 The Inst. of Min. and Metall. pp. 663-675
- [4] Dvornicenko D.I. et al.: Introduction of the agent IM 50 to the flotation of RE-ores. Cvetnye Metally, Moskva 1974/2 p. 80
- [5] Andresen, L.; Zahr, P.: Possibilities of processing the complex iron ore of Baotou. Erzmetall 39(1986) No 5 pp. 240-247
- [6] Wu Xianglin, Huang Linxuan: A study of hydroxamic acid for the flotation of RE-minerals. Proc. of the Int. Conf. on RE Devel. and Appl., Bejing, Sept. 10-14, 1985, Vol.I pp. 71-74
- [7] Meng Ying: Flotation of RE minerals from Bayun Ebo complex iron ore. Proc. of the Int. Conf. on RE Devel. and Appl., Bejing, Sept. 10-14, 1985, Vol.I pp. 79-82
- [8] Xu Xuefang: A new collector for bastnaesite 804 and a preliminary analysis of its flotation capabilities. Proc. of the Int. Conf. on RE Devel. and Appl., Bejing, Sept. 10-14, 1985, Vol.I pp. 75-78
- [9] Merker, G., Lesch, L.: Processing investigations for the exploration of the RE-deposit Dong Pao. Unpublished report of the Institute of Raw Materials Dresden, 1986
- [10] Melzer, Ch. et al.: Experimental study magnetic separation RE-ore Vietnam. Unpublished report of FIA Freiberg, 1990
- [11] Merker, G.: Breaking-off-report RE Dong Pao. Unpublished report of the Institute of Raw Materials Drecden, 1990
- [12] Schulz, G.: Development of a wet-mechanical processing technique for RE-ores from Vietnam. Unpublished report of FIA Freiberg No 1625, 1988
- [13] Gross, D., Ziegenbalg, S.: A technique for bastnaesite drying. Unpublished report of the Research Institute of Non-ferrous Metals Freiberg, 1988
- [14] Cichos, Ch. et al.: Flotation of the RE-ore Vietnam. Unpublished report of FIA Freiberg No 6509, 1990
- [15] Richter, H. et al.: Technique for treating bastnaesite concentrates. Patent DD 262 845 A1, C 01 F 17/00, 1986
- [16] Merker, G.: Bastnaesite/fluorite separation and biological leaching. Unpublished report of the Institute of Raw Materials Dresden, 1988