

THE APPLICATION OF FLORREA 8920, A NEW HYDROXAMATE-BASED FLOTATION COLLECTOR FOR THE FLOTATION OF RARE EARTH MINERALS

A. Jordens¹, Y. Zhiyong², and *F. Cappuccitti³

*¹Department of Mining and Materials Engineering, McGill University
Montreal, Quebec, Canada H3A0C5*

*²Shenyang Florrea Chemicals Co., Ltd
RM 1719, BLDG B, Hai-Li-De Mansion, No. 135, Chang-Jiang Street,
Huang-Gu District, ShenYang, LiaoNing Province
P.R. China*

*³Flottec, LLC
338 West Main Street,
Boonton, NJ, USA 07005*

**Corresponding author: fcappuccitti@flottec.com*

ABSTRACT

IMBSRE, one of the largest rare earth element (REE) producers in China, produces a rare earth oxide (REO) concentrate as a by-product by floating the middlings stream from a low intensity magnetic separation step in the main iron ore processing stage. As the mine depth has increased, flowsheet changes in the main iron ore circuit have reduced the REO grade and increased the magnetite to REO ratio in the middling product used as flotation feed for the REO circuit. Extensive laboratory work was carried out and identified a new modified hydroxamic acid product, Florrea 8920, that could provide better metallurgical results over the standard hydroxamic acid used as the main collector. This paper briefly reviews the use of hydroxamates in the flotation of oxide minerals, provides detailed information on the different hydroxamates available from Florrea and then provides a case study of the successful implementation of the Florrea 8920 product in a commercial Chinese REE flotation plant. The case study consists of a one year program of pilot plant testing and industrial trials to confirm the results of laboratory tests. The implementation of the new collector resulted in an improvement in grade and recovery to 61% and 64% respectively. The new collector also provided significant economic and environmental benefits.

KEYWORDS

Rare Earth Elements, Hydroxamic Acid Collector, Flotation

INTRODUCTION

The flotation of rare earth element (REE) bearing minerals is a topic which has been dominated in the English language literature by the work conducted on the Mountain Pass bastnäsite deposit (Pradip, 1981; Fuerstenau, Pradip, Khan, & Raghavan, 1982; Pradip & Fuerstenau, 1983, 1985, 2013; Fuerstenau & Pradip, 1991; Fuerstenau, Pradip, & Herrera-Urbina, 1992; Herrera-Urbina, Pradip, & Fuerstenau, 2013). By far the most important collector type used for the flotation of rare earth minerals (REM) is hydroxamates. These reagents were initially extensively described as REM collectors in the english literature by Pradip (1981) however they have been used successfully applied to numerous other minerals such as: cassiterite (Sreenivas & Padmanabhan, 2002); pyrochlore (Gibson, Kelebek, Aghamirian, & Yu, 2015); hematite, chrysocolla, rhodonite, hubnerite and pyrolusite (Fuerstenau, 2005); and malachite (Lenormand, Salman, & Yoon, 1979) amongst others.

The mechanism of flotation using hydroxamate collectors has been explained as the interaction of the reagent with dissolved metal cations from the mineral surface, followed by readsorption of the collector-metal complex to the mineral surface (Assis, Montenegro, & Peres, 1996; Fuerstenau, 2005). Important factors in the successful use of hydroxamates to float a given mineral include mineral solubility, the chelate stability of the reagent with the metal cations in the mineral of interest, the speciation of the dissolved metal species, the pKa of the reagent, and the chain length of the collector (Fuerstenau, 2005). The selectivity of oxhydryl collectors such as hydroxamates (reagents with a functional group consisting of oxygen atoms) has been explained by Nagaraj (1988) to be due to differences in the available electron density at the functional group. The available electron density in an oxhydryl collector is dependent on the atoms directly adjacent to the oxygen functional group (*e.g.* a nitrogen atom draws more of the electron density than a carbon atom, explaining the increased selectivity of hydroxamates over carboxylic acids), as well as the hydrophobic chain length of the collector molecule.

The development of hydroxamates as flotation collectors began in English language literature with a patent by Fuerstenau and Peterson (1969) highlighting the ability of alkyl hydroxamic acids to selectively recover iron oxide and chrysocolla minerals. In the following years from 1970 to the late-1980's hydroxamate synthesis processes relied on toxic, flammable solvents and suffered from low product yields and slow reaction times (Wang & Nagaraj, 1989). During this time period investigators in Russia experimented with the introduction of surfactants to the solvent-based synthesis process to improve yields (Wang & Nagaraj, 1989). An additional patent was granted during this time period to Yoon and Hilderbrand (1986) for the application of alkyl hydroxamates to remove Ti-impurities from kaolin clays however this patent demonstrated limited improvements in hydroxamate synthesis.

The patent by Wang and Nagaraj (1989) presented a significant technological breakthrough, as a refined hydroxamate synthesis process, using an aqueous mixture of alcohol and surfactant as solvent, improved reaction rates and yields such that commercially produced hydroxamate collectors could now contain up to 35% hydroxamate. This invention had a dual benefit as the presence of alcohol and surfactants in the final hydroxamate product was believed to improve frothing characteristics of this reagent (Wang & Nagaraj, 1989). Shortly thereafter, the same author was granted an additional patent describing the potential application of mixed collector systems (xanthate + hydroxamate) for the flotation of precious metal-bearing sulfide ores (Nagaraj, 1992).

The modern era of commercial hydroxamate production began in 2006 when Hughes (2006) was granted a patent for a hydroxamate synthesis route that employed only an aqueous solvent. This process, occurring under alkaline conditions, does not require surfactants, however the initially available paste formulations were difficult to handle for flotation operators (Hughes, 2006). This has since been addressed with the reagents now available in liquid form, containing 30% hydroxamate. A summary of the currently commercially available hydroxamate chemistries may be seen in Table 1.

Table 1 – Summary of commercially available hydroxamate chemical structures

Hydrophobic Group	Chemical Formulation
Alkyl	8 carbon straight chain salt
	8 carbon straight chain acid
Aromatic	Benzoic
	Salicylic
	Naphthenic
	Styrene

From the late 1990's onwards different Chinese research groups have conducted experimental work to advance reagent synthesis by decreasing costs and improving the handling of the final products. The results from this research can be seen in the five different hydroxamate reagents supplied by Florrea. Florrea supplies both aromatic and alkyl formulations. These reagents are available as hydroxamate salts in dry powder form with the alkyl products supplied as hydroxamate salts dissolved in alcohol. Details of the reagents along with information on reagent formulation and suggested usage are provided in Table A1 of the appendix of this paper. The Florrea products include reagents with a range of pKa values from 7.4 to 9.7 and are available with a significantly higher hydroxamate content (50–60%) than was previously possible. Importantly, the hydroxamates available from Florrea are also prepared in very stable formulations, improving shipping distances as well as the workplace environment for flotation operators due to the reduced presence of volatile solvents. The goal of this paper is to present as much detailed information as possible on the hydroxamates available from Florrea as well as highlight a successful application of the F8920 collector at a REM mine in Zhijin, China.

EXPERIMENTAL

The research presented in this paper is a collection of data from internal reports produced by Florrea during testing both at the industrial mine and in the laboratory. A portion of this data has previously been published in the Chinese literature by Zhang Qian, Zhang Jie, Chen Xiaohu, and Junyao (2003) and Tu Xiang and Liao Liew En (2003). The results of this research are presented here as an example of an industrial application of commercially available hydroxamic acids in the Chinese rare earth mineral (REM) industry.

Plant trials were conducted in the existing flotation circuit at the plant and laboratory tests were conducted in a 1.0 L XFD 63 single tank flotation cell. Specific conditions such as pH and reagent dosages are highlighted in the results section where applicable. Reagents used include sodium silicate as a depressant, F8920 (a modified aromatic hydroxamic acid collector) as collector and Flottec F100 (pine oil) as frother. Unfortunately specific information on the composition of the original collector used in the plant was not available however it was identified as a hydroxamic acid type collector. Typical conditioning times and reagent addition order for laboratory tests were addition of sodium silicate (6 min conditioning), addition of F8920 (3 min conditioning) and finally the addition of F100 (2 min conditioning). Flotation tests were conducted at 50–75°C and 40–70% solids.

The feed for the REM flotation circuit, used in all research work presented here, was the non-magnetic product of a low intensity magnetic separation stage used to remove ferromagnetic iron oxide minerals such as magnetite.

RESULTS AND DISCUSSION

The particle size distribution of three different samples of the flotation feed may be seen in Figure 1 where the P₈₀ of the flotation feed is in the range of approximately 25-35 µm. The fine size of this flotation feed results in high collector consumption, emphasizing the need for highly selective reagents.

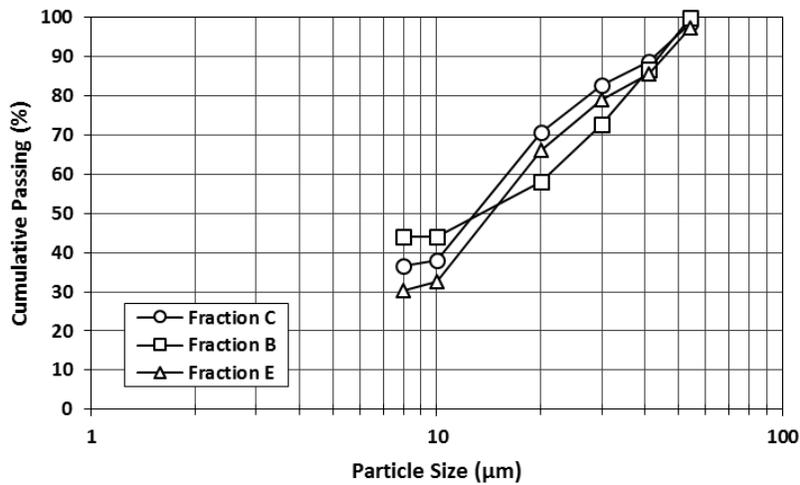


Figure 1 – Cumulative passing size for three different samples of the flotation feed used in this testwork

The composition of the feed material may be seen in Figure 2 with both total elemental content of each product as well as an indication of which minerals carry the elements. Also shown is the composition of a typical flotation concentrate. The data from Figure 2 indicates that the primary REMs in this feed are bastnäsite and monazite with a number of iron-bearing gangue minerals present in the feed. The REO grade of the concentrate as shown is approximately 61% indicating that the REM concentrate produced is very high grade (the typical REO content of monazite and bastnäsite varies from approximately 55–75%) (Anthony, Bideaux, Bladh, & Nichols, 2001).

Figure 3 shows cumulative grade versus cumulative recovery results for initial plant testwork comparing the original collector to F8920. The results shown indicate that F8920 produces comparable performance to the original collector while only requiring half the dosage of the original collector. The plant trial result shown in Figure 3 corresponds to a month of production and is the same product as the flotation concentrate shown in Figure 2. This trial was deemed successful as it exceeded grade and recovery targets for the plant with a reagent which was more stable and easier to handle by operators. Reports from the plant indicate that over a year the reagent substitution resulted in savings of up to 4 million USD.

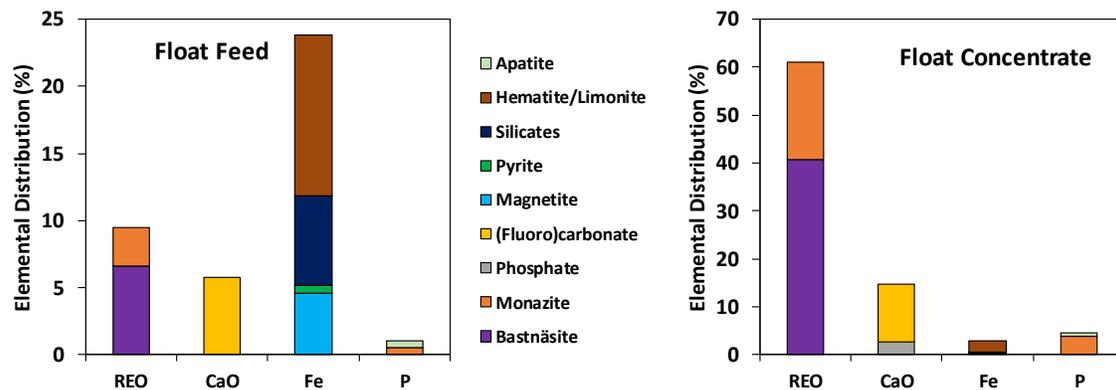


Figure 2 – Elemental distribution of the major elements present in the flotation feed and flotation concentrate, divided amongst the various contributing minerals and normalized to the total mass

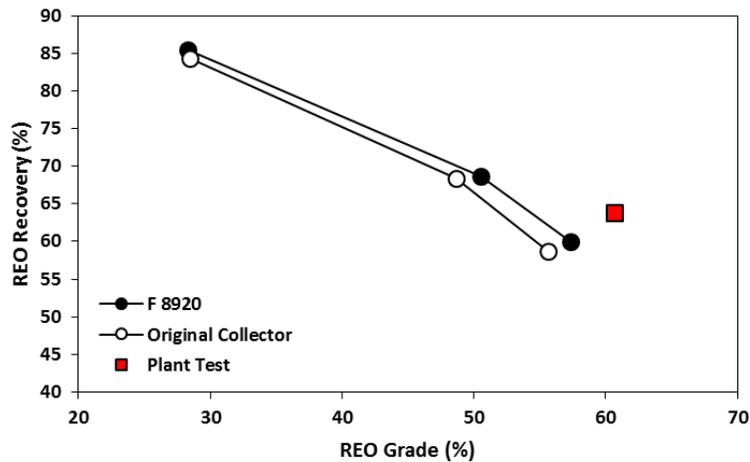


Figure 3 – Comparison of the F8920 collector to the original hydroxamic acid used in the plant. Grade-recovery curve constructed by considering the results for a final cleaned product as well as multiple middlings products produced from different stages of cleaning. Circles represent laboratory testwork and the square represents a one month plant trial

Dosage Determination

Further work to determine the effect of each reagent on the process and to select optimum dosages of all reagents was conducted in the laboratory by varying the dosage of depressant, collector and frother to determine the effect on both REO grade and recovery. The results may be seen in Figure 4. The selected optimum dosages for each reagent were identified by selecting the maximum REO recovery achieved. It is important to note that the grades shown here are representative of laboratory batch experiments, therefore the grades will not correspond with plant results from Figure 3 (multiple flotation stages are necessary to achieve concentrate grade).

The effect of sodium silicate dosage is shown in Figure 4a where increasing depressant dosage increases REO recovery. This may be due to blocking hydroxamate adsorption onto gangue minerals, thereby providing additional collector for REM collection. A potentially more significant explanation may be the impact of pH changes associated with depressant addition. For each 0.5 kg/t increase, the pH increased by 0.5 (from 7.5 to 9.0 for the range investigated in Figure 4a). This is significant as hydroxamate performance can be very sensitive to pH.

The effect of hydroxamate (F8920) dosage is shown in Figure 4b with dosages above 2.0 kg/t resulting in slight decreases in recovery. REO grade drops consistently with increasing collector addition, likely due to increased gangue recovery. The effect of frother shown in Figure 4c highlights the importance of cell hydrodynamics to maximize mineral recovery. Without proper gas dispersion (*i.e.* sufficient frother dosage) the recovery suffers significantly as there is insufficient bubble surface area available for particle collection. The final selected optimum dosages from batch flotation experiments were 4.0 kg/t sodium silicate, 2.0 kg/t F8920 and 0.075 kg/t F100 at a pH of ~8.5 determined by the sodium silicate addition. This corresponds well with the pKa range of F8920 (Table A1).

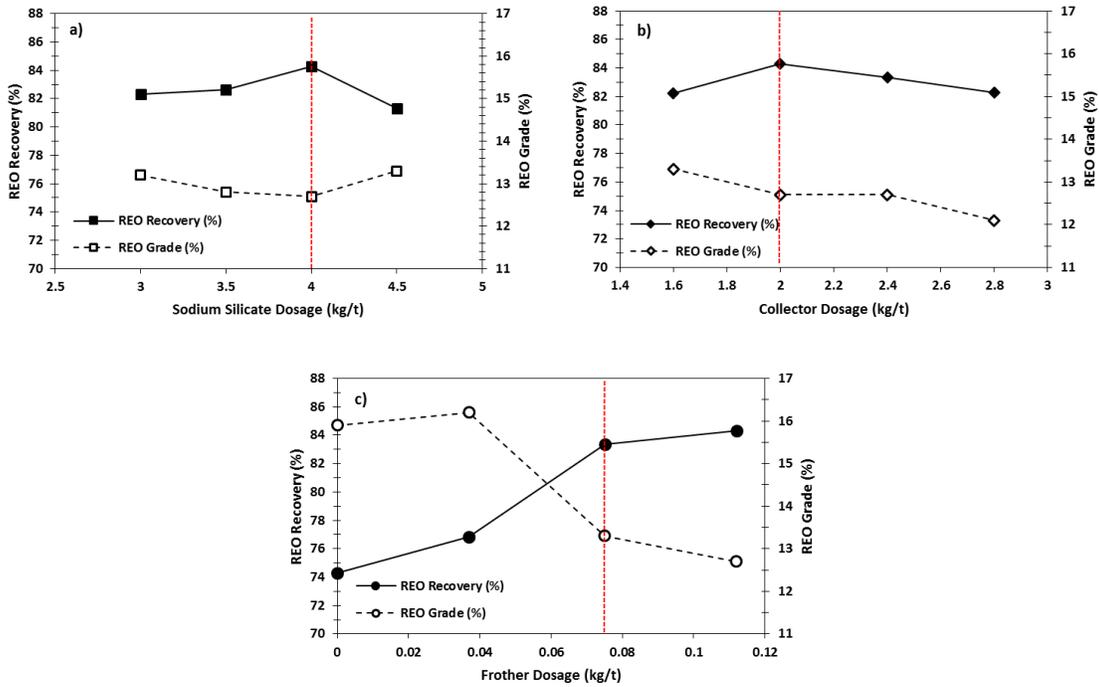


Figure 4 – Comparison of REO grade and recovery as a function of: a) Sodium Silicate dosage, b) Collector (F8920) dosage, and c) Frother (F100) dosage. Constant dosages of 4.0 kg/t sodium silicate (b, c), 2.0 kg/t F8920 (a, c) and 0.112 kg/t F100 (a,b). Dashed vertical lines indicate the dosages selected for further experimental work

Effect of Feed REO Grade and Feed Fe Grade

Additional laboratory batch flotation tests were conducted to determine the effect of changes in feed composition (REO grade and iron grade) on flotation using F8920. The results of these tests are shown in Figure 5. In particular, the impact on concentrate grade due to changes in feed grade are important and the effect of increasing REO feed grade in Figure 5a show a corresponding increase in concentrate grade as expected. The effect of changing iron grade in Figure 5b surprisingly shows little impact on concentrate grade, in spite of the fact that iron is known to bind preferentially with hydroxamates. This result may be explained by the fact that the low intensity magnetic separation stage upstream of the flotation circuit removes much of the ferromagnetic iron oxide minerals so that much of the remaining iron in the feed may be locked in relatively insoluble iron silicate minerals.

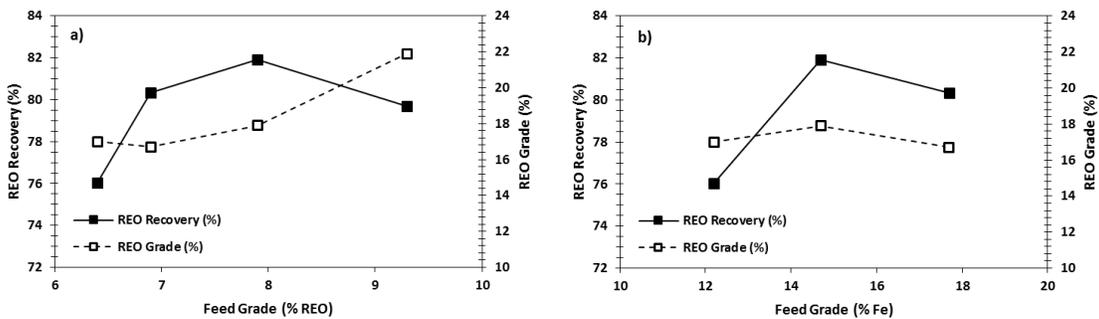


Figure 5 – Comparison of REO grade and recovery as a function of: a) Feed REO grade, b) Feed Fe grade

Effect of Plant Recycle Water

The effect of water quality was also tested in a laboratory setting with a single stage rougher followed by three stages of cleaning. The cumulative grade and recovery curve produced from these tests can be seen in Figure 6. The effect of using recycled water actually slightly improves the process by increasing REO grade, potentially indicating the possibility of lower than expected reagent consumption in the plant environment. The total reagent consumptions using recycled water were 2.8 kg/t sodium silicate, 1.90 kg/t F8920 and 0.374 kg/t frother. A schematic diagram of the flotation process using recycled water may be seen in Figure 7 including reagent dosages, conditioning times, mass pulls, recoveries and grades through all flotation stages. It can be seen that significant cleaning is required in order to achieve acceptable REO concentrate grades. Additionally, Figure 7 highlights the necessity of staged additions of hydroxamate collectors to achieve acceptable REO grades.

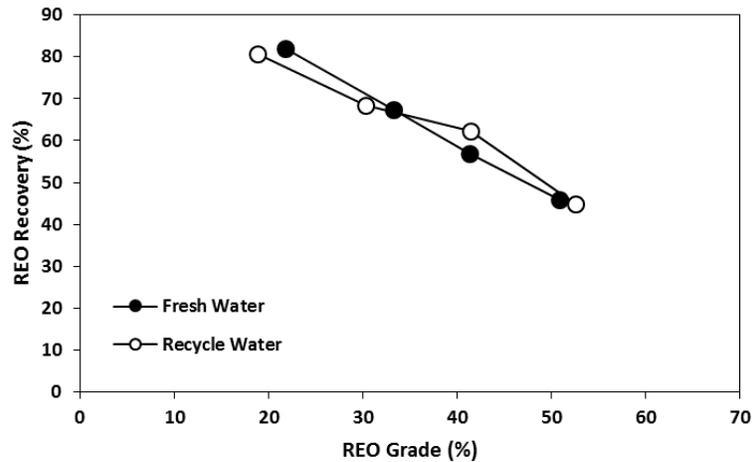


Figure 6 – Comparison of cumulative grade and recovery results for tests using fresh water versus recycled plant process water. Grade-recovery curve constructed by considering the results for a final cleaned product as well as multiple middlings products produced from different stages of cleaning

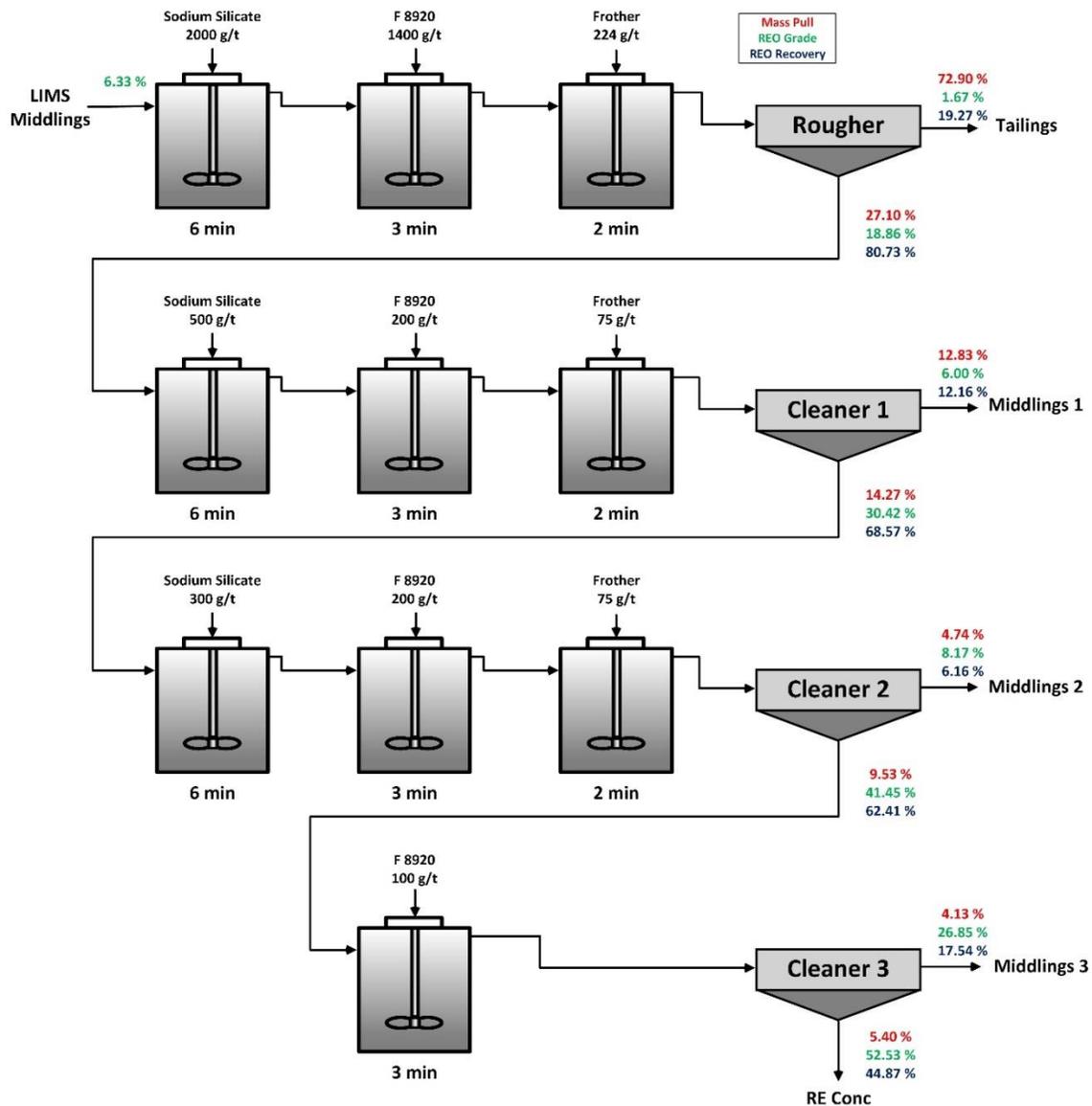


Figure 7 – Example flowsheet of the testwork conducted during the evaluation of the F8920 collector. For each stream percentage values represent, in descending order, mass pull, REO grade and REO recovery

A final laboratory test of one rougher and two cleaner stages was conducted to compare the two collectors. Each condition was repeated three times at a temperature of 50°C and 60% solids. The dosages for the tests using the original collector were 3.58 kg/t sodium silicate, 2.17 kg/t collector and 0.35 kg/t frother. For the F8920 test the dosages were 3.58 kg/t sodium silicate, 2.67 kg/t collector and 0.45 kg/t frother. While the F8920 test required a slightly higher consumption of collector and frother the use of this reagent is still preferred due to its formulation and stability. The results of the final comparative test shown in Figure 8 also indicate a significant improvement in REO recovery while still achieving concentrate grade. It should be noted that the grade in the laboratory tests is lower than that shown in Figure 3 which is to be expected as the laboratory flotation arrangement is only an approximation of the industrial process.

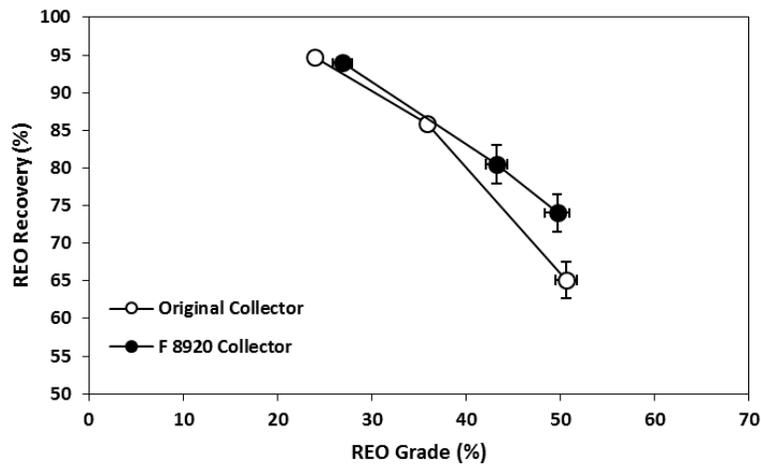


Figure 8 – Comparison of cumulative grade and recovery results for the original collector as well as the F8920 collector. Grade-recovery curve constructed by considering the results for a final cleaned product as well as multiple middlings products produced from different stages of cleaning. Error bars represent one standard deviation

CONCLUSIONS

This work has presented information on the hydroxamate collectors available from Florrea as well as presenting the results of an industrial application of one of these collectors, F8920. The conclusions are as follows:

- The collector F8920 was successfully implemented in a flotation circuit treating the non-magnetic stream from low intensity magnetic separation. The main REM components of the feed were bastnäsite and monazite. F8920 offered slightly improved metallurgical response to the existing hydroxamate collector used in the plant while also providing improvements in reagent stability and reagent handling.
- The dosages of sodium silicate, F8920 and F100 frother had a pronounced effect on the performance of laboratory flotation tests. The optimum dosage determined from lab tests for this ore were 4.0 kg/t sodium silicate, 2.0 kg/t F8920 and 0.075 kg/t F500. The effect of sodium silicate addition on pH is an important consideration in evaluating the impact of this reagent.
- Increases in feed REO grade resulted in a clear increase in REO concentrate grades, conversely the REO grade of the concentrate was relatively insensitive to the feed Fe content. It is speculated that this is due to the Fe occurring in relatively insoluble Fe-silicate minerals.
- The use of recycled water in this system showed no negative impact on metallurgical performance and actually results in a slight decrease in reagent consumption compared to the use of fresh water.
- The flotation circuit requires multiple stages of cleaning with corresponding staged additions of collector in order to achieve acceptable concentrate REO grade.

ACKNOWLEDGMENTS

The authors would like to acknowledge Flottec and Florrea for their assistance in gathering the information presented here and for the permission to publish this work.

REFERENCES

- Anthony, J. W., Bideaux, R. A., Bladh, K. W., & Nichols, M. C. (2001). Handbook of Mineralogy. Retrieved July 16, 2012, from Mineralogical Society of America <http://www.handbookofmineralogy.org/>
- Assis, S. M., Montenegro, L. C. M., & Peres, A. E. C. (1996). Utilisation of hydroxamates in minerals froth flotation. *Minerals Engineering*, 9(1), 103-114.
- Fuerstenau, D. W., & Pradip. (1991). The role of inorganic and organic reagents in the flotation separation of rare-earth ores. *International Journal of Mineral Processing*, 32, 1-22.
- Fuerstenau, D. W., Pradip, & Herrera-Urbina, R. (1992). The surface chemistry of bastnaesite, barite and calcite in aqueous carbonate solutions. *Colloids and Surfaces*, 68, 95-102.
- Fuerstenau, D. W., Pradip, Khan, L. A., & Raghavan, S. (1982). *An Alternate Reagent Scheme for the Flotation of Mountain Pass Rare-Earth Ore*. Paper presented at the XIV International Mineral Processing Congress, Toronto.
- Fuerstenau, M. C. (2005). *Chelating Agents as Flotation Collectors*. Paper presented at the Innovations in natural resource processing: proceedings of the Jan D. Miller symposium, Salt Lake City, USA.
- Fuerstenau, M. C., & Peterson, H. D. (1969). USA Patent No. 3438494. U. S. P. Office.
- Gibson, C. E., Kelebek, S., Aghamirian, M., & Yu, B. (2015). Flotation of pyrochlore from low grade carbonatite gravity tailings with benzohydroxamic acid. *Minerals Engineering*, 71, 97-104.
- Herrera-Urbina, R., Pradip, & Fuerstenau, D. W. (2013). Electrophoretic mobility and computations of solid-aqueous solution equilibria for the bastnaesite-H₂O system. *Minerals and Metallurgical Processing*, 30(1), 18-23.
- Hughes, T. C. (2006). AU Patent No. 7049452. U. S. P. Office.
- Lenormand, J., Salman, T., & Yoon, R. H. (1979). Hydroxamate flotation of malachite. *Canadian Metallurgical Quarterly*, 18, 125-129.
- Nagaraj, D. R. (1988). The chemistry and application of chelating or complexing agents in minerals separations. In P. Somasundaran & B. M. Moudgil (Eds.), *Reagents in Mineral Technology* (Vol. 27). New York, USA: Marcel Dekker.
- Nagaraj, D. R. (1992). USA Patent No. 5126038. U. S. P. Office.
- Pradip. (1981). *The Surface Properties and Flotation of Rare-Earth Minerals*. (PhD Thesis), University of California, Berkeley, Berkeley.
- Pradip, & Fuerstenau, D. W. (1983). The Adsorption of Hydroxamate on Semi-Soluble Minerals. Part I: Adsorption on Barite, Calcite and Bastnaesite. *Colloids and Surfaces*, 8, 103-119.
- Pradip, & Fuerstenau, D. W. (1985). Adsorption of hydroxamate collectors on semi-soluble minerals. Part II: Effect of temperature on adsorption. *Colloids and Surfaces*, 15, 137-146.
- Pradip, & Fuerstenau, D. W. (2013). Design and development of novel flotation reagents for the beneficiation of Mountain Pass rare-earth ore. *Minerals and Metallurgical Processing*, 30(1), 1-9.
- Sreenivas, T., & Padmanabhan, N. P. H. (2002). Surface chemistry and flotation of cassiterite with alkyl hydroxamates. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 205, 47-59.
- Tu Xiang, & Liao Liew En. (2003). Separation Technology of the Rare Earth Elements (Chinese). *Guizhou Chemical Industry*, 28(3), 3-5.

Wang, S. S., & Nagaraj, D. R. (1989). USA Patent No. 4871466. U. S. P. Office.

Yoon, R. H., & Hilderbrand, T. M. (1986). USA Patent No. 4629556. U. S. P. Office.

Zhang Qian, Zhang Jie, Chen Xiaohu, & Junyao, H. (2003). Selection of Beneficiation Technology for Zhijin Rare Earth Containing Phosphorous Ore in Guizhou (Chinese). *METAL MINE*, 321, 23-25.

APPENDIX

Table A1 – Information on formulations and typical usage for the five hydroxamate collectors available from Florrea

Formulation			Usage				
Reagent Name	Chemical Structure	Hydroxamate Content	Solubility	pKa	pH Range	Typical Dosage (g/ton)	Applications
F7510	Modified aromatic hydroxamic acid	~50 %	Soluble in hot water Soluble in alcohol, slightly soluble in ether	8.1-8.9			Smithsonite Wolframite Scheelite Cassiterite Ta and Nb minerals
F8005	Alkyl Hydroxamic Acid	~60 %	Sparingly soluble in water Soluble in some organic solvents	9.4-9.7		10-1000	Copper oxides Hematite Wolframite Scheelite Ilmenite Ta and Nb minerals REE minerals Oxidised base metal sulphides
F8103	Alkyl Hydroxamic Acid	~60 %	Soluble in water Solubility increases with increasing pH	9.4-9.7	4-10.5	50-1000	Copper oxides Hematite Wolframite Scheelite Cassiterite Ilmenite Nb minerals REE minerals Oxidised PGM-bearing base metal sulphides Other oxide minerals (Be, Zr, Hf, Ta, U)
F8905	Modified aromatic hydroxamic acid	~50 %	Sparingly soluble in water Soluble in aqueous alkaline solutions	7.4-8.9	5-9		Cassiterite (main application) Wolframite Scheelite Copper oxides Hematite REE minerals Other oxide minerals (Cu, Fe)
F8920	Modified aromatic hydroxamic acid	~50 %	Insoluble in water	7.4-8.9	8-8.5	50-1000	REE minerals Other oxide minerals