Study of pyrochlore matrix composition effects on froth flotation by SEM–EDX

S. Chehreh Chelgani [a,*], B. Hart [a], J. Marois [b], M. Ourriban [b]

[a] Surface Science Western, Research Park, University of Western Ontario, London, Ontario, Canada N6G 0J3
[b] Niobec Inc., 3400 ch. du Columbium, St-Honoré-de-Chicoutimi, Québec, Canada G0V 1L0

ARTICLE INFO

ABSTRACT

Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM–EDX) was used to analyse pyrochlore grains from Niobec froth flotation plant. Approximately 200 pyrochlore gains from the mill feed, pyrochlore rougher feed, pyrochlore rougher concentrate, and tail were analysed in order to identify a potential relationship between pyrochlore matrix composition and selective separation. Analyses indicate that pyrochlore grains with high Fe content appear to be less recoverable than those with a lower Fe content. Furthermore, analysis indicates that the flotation response is related to matrix Fe rather than Fe occurring as inclusions within the pyrochlore. These mineralogical investigation results are from a much larger program where pyrochlore matrix composition will be examined in relation to surface chemistry and flotation selectivity.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Niobium is used as an alloying agent predominantly in the steel production industry. Niobium-containing super alloys are used in the construction of jet and rocket engines because of their temperature stability properties. Superconducting alloys containing Nb along with titanium and tin are widely used in MRI scanners. Other applications include welding, nuclear industries, electronics, optics, numismatics and jewellery. The predominant niobium bearing minerals are pyrochlore and columbite (Tanabe, 2003; Belzile, 2009).

Pyrochlore deposits contain substantial amounts of carbonates, sulphides, and other gangue minerals such as biotite, apatite, and feldspar. In almost all pyrochlore processing operations, after mining and comminution, the ore body is subjected to desliming to remove particles finer than 10 μm. The deslimed mineral pulp is subjected to three stages of flotation. The first stage involves flotation of carbonates which removes a significant proportion of the feed without much loss of pyrochlore. The tail of carbonate flotation is then subjected to pyrochlore flotation. The froth at this stage not only contains pyrochlore but also some sulphides, such as pyrite and pyrrhotite, which are removed by reverse flotation in the next processing stage (Burks, 1958; Shapolov and Polkin, 1958; Zakharov et al., 1967; Razvozzhaev and Nikiforov, 1972; Bogdanov et al., 1973; Abeidu, 1974; Raby and Desrochers, 1975; Wilson, 1979; Biss and Nadeau, 1982; Biss, 1985).

The largest pyrochlore deposit is the CBMM mine located south of Araxá, Minas Gerais, followed by the Catalão mine east of Catalão, Goiás, in Brazil. The third largest deposit of niobium ore is the Saint-Honore mine west of Saint-Honore near Chicoutimi, Quebec (Kouptsidis et al., 2008). Since 1974 Niobec has been extracting niobium from the St-Honoré carbonatite deposit. Niobec is the only operating Nb extraction facility in North American and one of the three major world producers of ferroniobium (Dufresne and Goyette, 2004; Belzile, 2009).

In the St-Honoré carbonatite ore, pyrochlore represents only about 1% of the total mineral mass. The dominant minerals are carbonates (mainly dolomite and calcite), silicates (biotite, chlorite and Na/K-feldspars) and to a lesser extent apatite. Other constituent minerals include magnetite, hematite, pyrite and zircon (Dufresne and Goyette, 2004).

With the aim of optimising the flotation process for the Niobec ore, experiments were performed on the influence of collector, activator and type of water on Nb_2O_5 recovery and grade in the rougher and cleaner concentrates (Gomez et al., 1987; Rao et al., 1988). During process development it became evident that mild cationic collectors were preferable to anionic collectors because of their ability to collect less calcite and dolomite. Electro-kinetic measurements showed pyrochlore surfaces to be negatively charged in the desired pH flotation range. In light of this, tallow diamine acetate was selected for pyrochlore flotation; addition rates were 220 g/t (Dufresne and Goyette, 2004; Belzile, 2009).

Along with the pyrochlore, tallow diamine floats all of the silicates, iron oxides, apatite, sulfides and part of the dolomite, but by gradually reducing the pH, and by introducing silicate depressant all of these except pyrite are depressed (Dufresne and Goyette, 2004). A series of tests were performed at various lower flotation pHs to assess selectivity and recovery. However, no significant improvement in selectivity was observed when the pH was
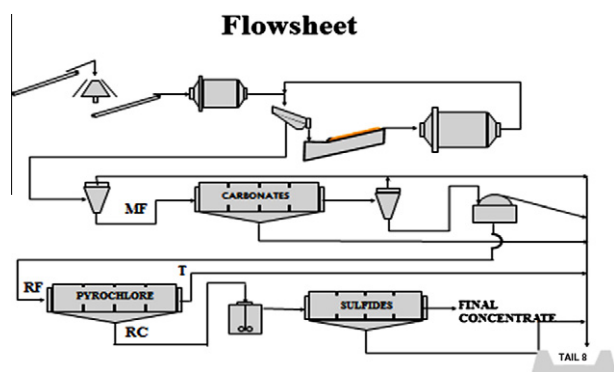
Fig. 1. Simplified flowsheet of the Niobec process. The feed (mill feed: MF), after size reduction, is subjected to carbonate flotation; the tails from carbonate flotation, refered to as the rougher feed (RF), is pumped to a pyrochlore flotation bank; the rougher concentrate (RC) is then sent through five countercurrent stages of cleaning; the cleaner concentrate (CC) is subjected to sulfide flotation. The rejects from the pyrochlore rougher banks and the cleaner circuit are sent to tailings (T) (Dufresne and Goyette, 2004).

reduced and therefore the pH was maintained between 6.8 and 7.5 (Rao et al., 1988; Dufresne and Goyette, 2004; Belzile, 2009).

A major difficulty of pyrochlore flotation results from the similar flotation characteristics (the same surface chemistry) of pyrochlore and its associated minerals (other oxides and silicates) (Gomez et al., 1987); selectivity cannot be achieved solely by choosing a single collector (Dufresne and Goyette, 2004). The basis of this difficulty is related to the similarity in the iso electric points (IEP) of pyrochlore and the main contaminant minerals (the IEP of charge for pyrochlore, biotite, pyrite and feldspar at potable water is 2.5, 2, 1.5 and 1.9, respectively (Gomez, 1987)) which limits selective flotation in response to electrostatic collector adsorption (Gomez et al., 1987; Rao et al., 1988).

There is significant evidence to support that surface chemical variability can be directly related to variability in matrix composition (Hu et al., 2003; Barros et al., 2008; Oelkers et al., 2009). In a paper looking at the surface chemistry of multi-oxide silicates, in particular the pyroxenes diopside and enstatite, Oelkers et al. (2009) identified (1) divalent metal loss was directly related to pH, highest in alkaline solutions and (2) the removal rate and amount of Mg was on the order of 2x greater in diopside relative to enstatite. In this instance the loss of divalent metals results in the creation of "internal" surface sites, some of which can become protonated. Furthermore, the loss of metal ions corresponds to a linear increase in protonation, the degree of which is a function of the mineral composition. The data indicates that, metal-proton exchange reactions play a major role in surface reactivity and that variability in surface reactivity is strongly linked to mineral composition. Given this example it would be reasonable to assume that similar relationships occur in compositionally variable pyrochlore grains where collector adsorption may be linked to variability in metal ion removal rates. Therefore, understanding collector attachment in relation to variable matrix chemistry and its expression on the pyrochlore surface will potentially aid in the development of collectors or reagent strategies towards, increasing selectivity, lowering reagent consumption, promoting improved Nb-recoveries, and finally leading to simpler circuits.

In this study, matrix compositions of pyrochlore grains from Niobec froth flotation circuit were investigated. The study utilised scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM–EDX) to measure concentrations of the main matrix elements in pyrochlore grains from the mill feed (MF), pyrochlore rougher feed (RF), pyrochlore rougher concentrate (RC), and pyrochlore rougher tail (T) (Fig. 1). The main aim of this study is to examine the pyrochlore matrix composition from various stream products with the potential to relate the matrix composition to variability in flotation recovery. This study is part of a much larger program investigating the link between pyrochlore surface and matrix chemistry and their effects on collector adsorption.

2. Experimental methodology

For the mineralogical investigation, pyrochlore grains were collected from various points in the flotation scheme at the Niobec plant. A simplified process flowsheet is shown in Fig. 1. Approximately two hundred pyrochlore gains were analysed from the mill feed (carbonate rougher feed), pyrochlore rougher feed (carbonate rougher tail), pyrochlore rougher concentrate, and pyrochlore rougher tail. The concentration of selected elements were measured in the pyrochlore grains with a LEO 440 SEM equipped with a Gresham light element detector and a Quartz XOne EDX system.

Table 1
Results of SEM analysis of pyrochlore grains in pyrochlore rougher feed and pyrochlore rougher concentrate at.%.

MF (%)	Minimum	Maximum	Mean	Std. deviation	RF (%)	Minimum	Maximum	Mean	Std. deviation
O	27.28	45.67	37.65	4.03756	O	26.15	52.2	40.17	4.87
F	*MLD	7.62	3.62	1.716626	F	*MLD	9.37	4.20	2.38
Na	0.23	7.04	3.45	1.414552	Na	0.1	8.56	4.50	1.59
Mg	*MLD	2.37	0.49	0.424494	Mg	*MLD	1.88	0.43	0.32
Ca	3.6	16.02	11.71	2.443935	Ca	1.15	15.53	10.35	2.53
Ti	0.82	3.58	1.82	0.738176	Ti	0.57	5.44	1.60	0.70
Fe	0.68	22.88	3.35	3.59002	Fe	*MLD	24.63	2.08	3.90
Sr	*MLD	5.13	2.55	0.961591	Sr	*MLD	6.13	2.55	1.00
Nb	25.33	43.02	35.40	3.433779	Nb	24.54	41.13	33.75	4.06
RC (%)	Minimum	Maximum	Mean	Std. deviation	Tail (%)	Minimum	Maximum	Mean	Std. deviation
O	31.98	54.03	40.24	5.05	O	28.77	48.41	39.656	7.78
F	*MLD	10.75	4.93	2.28	F	*MLD	6.81	2.022	2.82
Na	1.62	8.34	4.67	1.54	Na	0.4	4.16	2.436	1.84
Mg	*MLD	0.86	0.41	0.27	Mg	*MLD	1.36	0.642	0.54
Ca	5.88	20.26	11.17	2.51	Ca	2.15	14.97	7.382	5.11
Ti	0.63	3.84	1.62	0.61	Ti	0.98	2.7	1.75	0.64
Fe	0.48	4.87	1.53	1.07	Fe	1.39	30.44	11.024	12.54
Sr	0.64	4.78	2.59	0.86	Sr	1.21	2.7	1.916	0.67
Nb	21.94	40.91	32.88	4.57	Nb	24.02	40.37	31.858	5.80

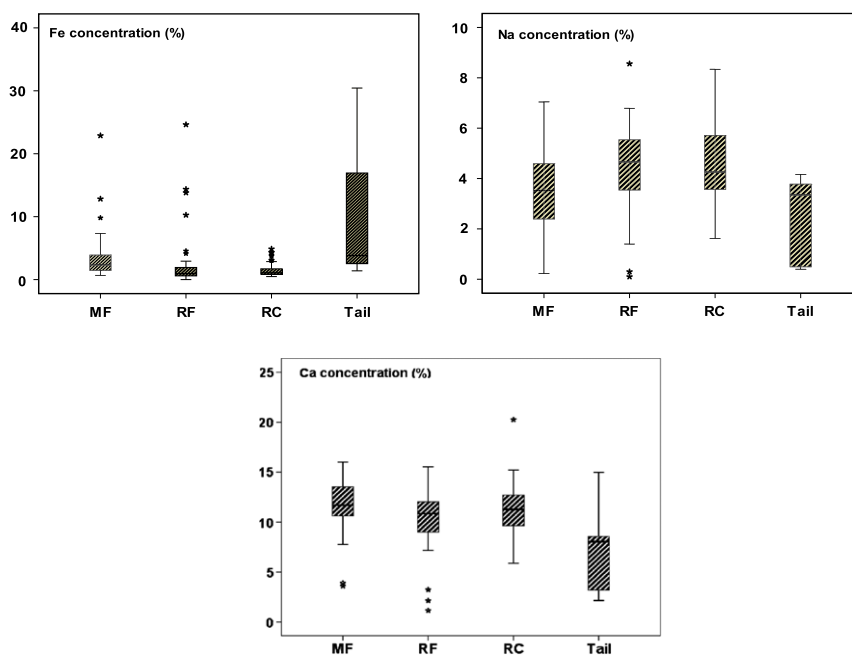* MLD = method detection limits, elements may be present but are below for detection.

Fig. 2. Comparison of Fe, Ca, and Na-concentration (%) mass signals of pyrochlore grains.

Table 2
Inter-correlation (Pearson correlation) between A site pyrochlore ($A_2B_5O_7$) elements. Inter-correlation is a measure of linear association between two variables. Values of the inter-correlation range from −1 to 1. The sign of the correlation indicates the direction of the relationship, and its absolute value indicates the strength, with larger absolute values indicating stronger relationships. A negative value for the correlation implies a negative or inverse association, where a positive value means a positive association.

Pearson correlation	Fe	Na	Sr	Ca
Fe	1.000	−.590	−.246	−.518

The instrument was operated at 20 kV, 400 pA. Samples were sputter-coated with Au/Pt in order to prevent charging during analyses.

3. Result and discussion

3.1. Pyrchlore structure

Pyrochlores ($A_2B_5O_7$) are complex oxides whose structures are made up of interconnected octahedra, consisting predominantly of Na, Ca, Fe and Sr in the A position and Nb, Ti, and Ta (B position). The various pyrochlore group end members are made by isomorphic substitution in the B position. Predictable variability in the proportion of A site ions results in minor compositional variability of the subgroups. Pyrochlore grains containing inclusions of Fe (presumably as an oxide) have also been identified (Hogarth, 1960, 1977; Petruk and Owens, 1975; Zurevinski and Mitchell, 2004).

The EDX analysis of pyrochlore grains from mill feed (MF), pyrochlore rougher feed (RF), pyrochlore rougher concentrate (RC), and pyrochlore rougher tail (T) are presented in Table 1. Analyses of pyrochlore grains from the RC and Tail samples show a relative decrease in matrix Na and Ca, along with a corresponding increase in Fe in grains from the tail (Fig. 2). These results suggest that the presence of iron in pyrochlore (either as an inclusion or structurally bound) may have an impact on its selectivity.

Given the observed relationship between Fe content and pyrochlore floatability, it was important to determine the whether
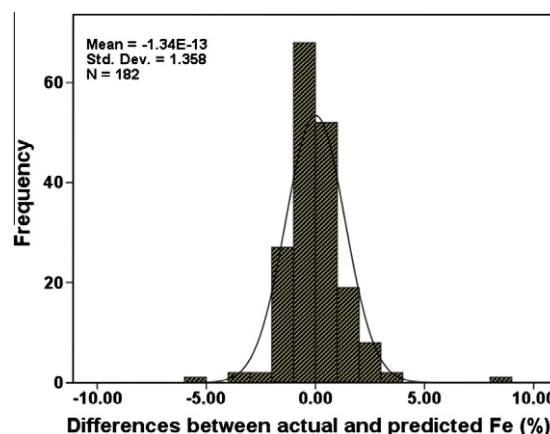

Fig. 3. Distribution of difference between actual and estimated Fe concentration from Eq. (2).

this relationship was due to Fe in the mineral matrix or related to potential inclusions within the mineral. In order to determine the nature of the Fe in the pyrochlore, statistical methods were performed on the analyses within the entire data set (MF, RF, RC, and T) in an attempt to distinguish matrix from inclusion iron. Inter-correlations between A site elements (Ca, Na, Fe, and Sr) indicate that higher Fe contents corresponds to lower amounts of Ca, Na and Sr (Table 2). In addition, the linear and non-linear enter-remove regression methods shows that the Fe content in Niobec pyrochlore grains is predictable with other A position elements (Eqs. (1) and (2)) where the difference between actual and non-linear predicted iron content for more than a hundred grains is less than%1 (Fig. 3).

$$Fe(\%) = 20.629 - 1.517Na - 0.942Sr - 0.856Ca \quad R^2 = 0.73 \quad (1)$$

$$Fe(\%) = 31.957 - 5.621Na + 0.953Na^2 - 0.056Na^3 - 3.965Ca$$
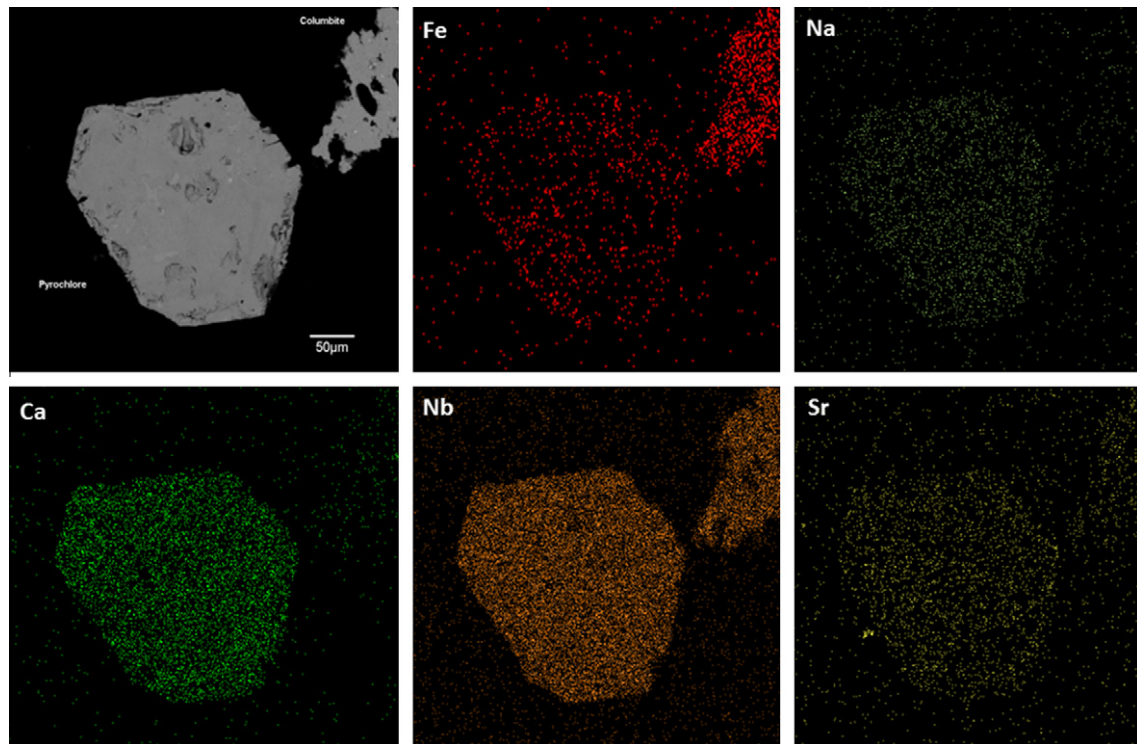$$+ 0.28Ca^2 - 0.007Ca^3 - 0.407Sr \quad R^2 = 0.88 \quad (2)$$

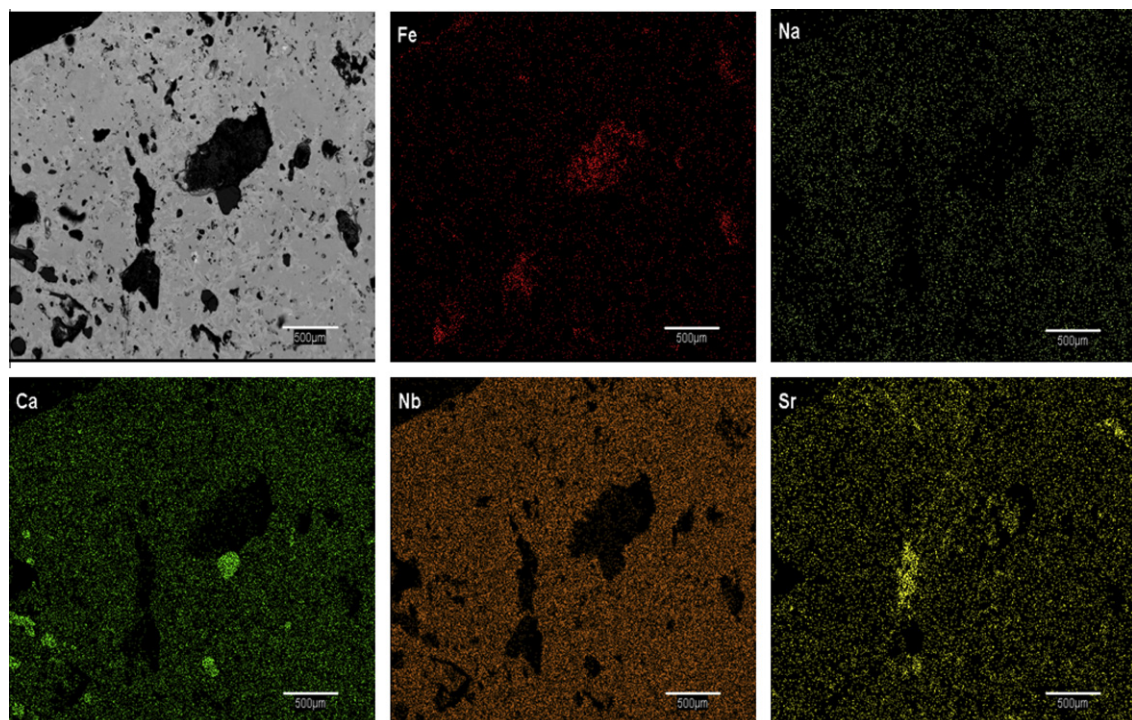Fig. 4. Element's distribution in a pyrochlore grain.

Fig. 5. EDX maps of a pyrochlore containing Fe as inclusions.

Both statistical methods theoretically corroborate that the Fe in pyrochlore is indeed a matrix member. A significant contribution to the Fe content in pyrochlore grains by inclusions would have resulted in poor inter-correlation data and large differences between the actual and non-linear predicted Fe values. EDX mapping of several cross sectioned pyrochlore grains supports the statistical analysis. The Fe map of the pyrochlore grain in Fig. 4 shows a relatively homogenous distribution across the grain, supporting the statistical analysis that Fe in the Niobec pyrochlore grains is predominantly matrix bound. For comparison EDX maps of a pyrochlore containing Fe as inclusions is included. Note the localised Fe regions identifying the Fe inclusions (Fig. 5).

These analyses indicate that a higher concentration of matrix Fe in pyrochlore grains can potentially be linked to poor selectivity. Given these observations we have identified two potential explanations for the results (1) the higher proportion of Fe decreases the relative negative surface charge on pyrochlore, potentially preventing the adsorption of the cationic amine collector (Barros et al. (2008) reported higher concentrations of iron in apatites, rendering the surface of the apatites positive or less negative in the weakly alkaline pH range inhibiting collector attachment) and (2) higher surface iron content could promote a greater degree of surface oxidation thereby interfering with collector adsorption (poor flotation of iron pyrochlore is noted in the plant (Rao et al., 1988)). These 2 scenarios potentially explain the results from the SEM–EDX study. Ongoing investigations linking pryochlore surface reactivity to the variability in matrix Fe content using surface analytical tools are currently underway. The results will be applied to testing scenarios designed to improve flotation recovery.

4. Conclusions

SEM–EDX analysis of pyrochlore grains has linked poor flotation performance to an increase in grain Fe content. Statistical analyses identified that the increase in Fe in the pyrochlore is not as a result of Fe rich inclusions, rather it has been identified as an increase matrix Fe content. Support for this conclusion is provided by EDX element mapping where the Fe in cross sectioned pyrochlore grains appears evenly distributed. The results suggest that poor floatability is related to higher matrix Fe contents. Two possible explanations linking high Fe content to poor recovery have been suggested: (1) high Fe content resulting in change in surface charge, (2) high Fe content resulting in a variable degree and rate of surface oxidation. In progress studies linking pryochlore surface reactivity using surface analytical tools are investigated. The results will be applied to testing scenarios designed to improve flotation selectivity.

Acknowledgment

References

Abeidu, A.M., 1974. Studies on the selective flotation of pyrochlore. Journal of Applied Chemistry and Biotechnology 24 (8), 425.
Barros, A.F.L., Ferreira, E.E., Peres, A.E.C., 2008. Floatability of apatites and gangue minerals of an igneous phosphate ore. Minerals Engineering 21, 994–999.
Biss, R., Nadeau, R., 1982. Direct flotation of pyrochlore. United States patent, p. 4342648.
Biss, R., 1985. Process for recovering pyrochlore mineral containing niobium and tantalum. United States patent, p. 4493817.
Belzile, E., 2009. Technical Report for Niobec Mine Quebec. Canada, NI, pp. 43–101.
Bogdanov, O.S., Yeropkin, Y.I., Koltunova, T.E., Khobotova, N.P., Shtchukina, N.E., 1973. Hydroxamic acids as collectors in flotation of wolframite, cassiterite and pyrochlore. In: Proceedings X International Mineral Processing Congress, IMM, London, UK, p. 533.
Burks, H.G., 1958. Separation of pyrochlore from calcite, apatite and silica. United States patent, p. 2951585.
Dufresne, C., Goyette, G., 2004. The production of ferronibium at the Niobec mine. Factory Report, pp. 1–7.
Gomez, R.E., Finch, J.A., Laplante, A.R., 1987. Effects of the type of water on the selective flotation of pyrochlore from niobec. Colloids and Surfaces 26, 333.
Gomez, R.E., 1987. Recovery of pyrochlore from slims discarded at Niobec by column flotation, p. 10.
Hogarth, D.D., 1960. A study of pyrochlore and betafite. The Canadian Mineralogist, p. 610.
Hogarth, D.D., 1977. Classification and nomenclature of the pyrochlore group. American Mineralogist 62, 403–410.
Hu, Y., Liu, X., Xu, Z., 2003. Role of crystal structure in flotation separation of diaspore from kaolinite, pyrophyllite and illite. Minerals Engineering 16, 219–227.
Kouptsidis, J., Peters, F., Proch, D., Singer W., 2008. Niob für TESLA, pp. 1–16.
Petruk, W., Owens, D.R., 1975. Electron microprobe analyses for pyrochlores from OKA, QUEBEC. The Canadian Mineraloglst 13, 282.
Oelkers, E.H., Golubev, S.V., Chairat, C., Pokrovsky, O.S., Schott, J., 2009. The surface chemistry of multi-oxide silicates. Geochemica et Cosmo. Acta 73, 4617–4634.
Raby, R., Desrochers, C.J., 1975. Pyrochlore flotation. United States patent, p. 3910836.
Rao, S.R., Gomez, R.E., Finch, J.A., Biss, R., 1988. Effect of water chemistry on the flotation of pyrochlore and silicate minerals. Mineral Engineering 1 (3), 189.
Razvozzhaev, Y.I., Nikiforov, K.A., 1972. Activation of pyrochlore during flotation of a chemical beneficiation cake. Scientific-Research Institute of Rare Metals, Irkutsk 2, 108.
Shapolov, G.M., Polkin, S.I., 1958. Flotation properties of pyrochlore, zirkon and associated minerals. Sborn. Nauch. Trud. Moscow, Inst. Tsvet. Metal Isolate 31, 256.
Tanabe, K., 2003. Catalytic application of niobium compounds. Catalysis Today 78 (1–4), 65–77.
Wilson, J.A., 1979. Flotation recovery of pyrochlore. United States patent, p. 4178235.
Zakharov, A.E., Ilie, P., Pol'kin, S.I., Solnyshkin, V.I., 1967. Reaction of sodium sulfide with pyrochlore, zircon, and monazite in flotation with sodium oleate. In: Plaksin, I.N. (Ed.), Flotation Properties of Rare Metals Minerals. Primary Sources, New York, USA, p. 71.
Zurevinski, S.E., Mitchell, R.H., 2004. Extreme compositional variation of pyrochlore-group minerals at the OKA carbonatite complex, quebec: evidence of magma mixing? The Canadian Mineralogist 42, 1159.