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Rare Earth Flotation Fundamentals: A Review

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ABSTRACT: *The United States contains a variety of domestic rare earth element mineral sources containing such as ancylite, bastnasite, monazite, and xenotime. Research has been performed to investigate the fundamental surface chemistry involved in the froth flotation of these minerals, and apply the knowledge gained to substantiate the results through experimental testwork on a domestically sourced rare earth ore. This paper will outline the fundamentals and literature of rare earth mineral flotation, review its industrial applications and provide some recent research updates.*

Keywords: *Flotation, rare earths, surface chemistry*

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I. THE RARE EARTH ELEMENTS

Rare earth elements (REE's) are a unique family of elements with nearly identical physical and chemical properties. They account for approximately 1/6th of all naturally occurring elements, but the entire group occupies only one position on the periodic table. These 15 elements make up the lanthanide series (atomic numbers 57–71), and all but one (promethium) occur naturally. In addition to these 15 elements, yttrium and scandium are also considered rare earths since they tend to occur in the same deposits as the rare earths and share similar physical and chemical properties as seen in Figure 1. In particular Figure 2 denotes, a cartoon of the subtle differences in each caused by the 4f atomic sub shell(Gschneidner Jr., 1964). These subtle differences result in very difficult challenges in the selective concentration and final separation of each rare earth. (Anderson, 2015, Kronholm, Anderson, Taylor, 2013)

Rare earths are separated into two different subsections; the "lights" or LREE's (lanthanum^{57} through europium^{63}) and the "heavies" or HREE's (gadolinium^{64} through lutetium^{71}). Yttrium is generally considered a heavy rare earth since its ionic radius is close to that of the HREE's, while scandium is not considered either a light or a heavy.

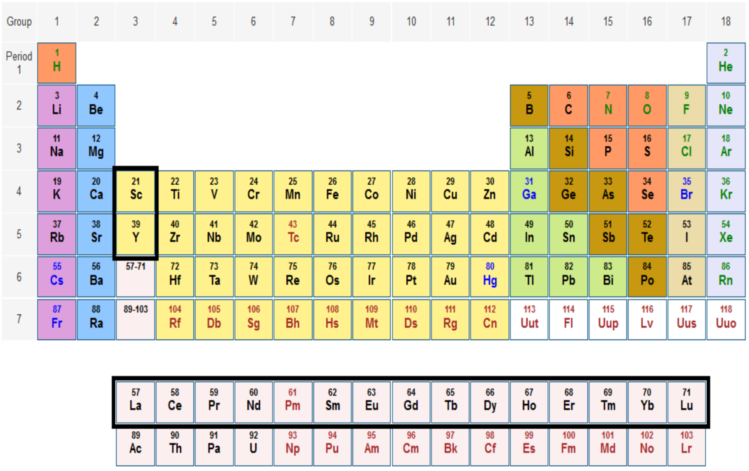


Figure 1–Rare Earth Elements on the Periodic Table

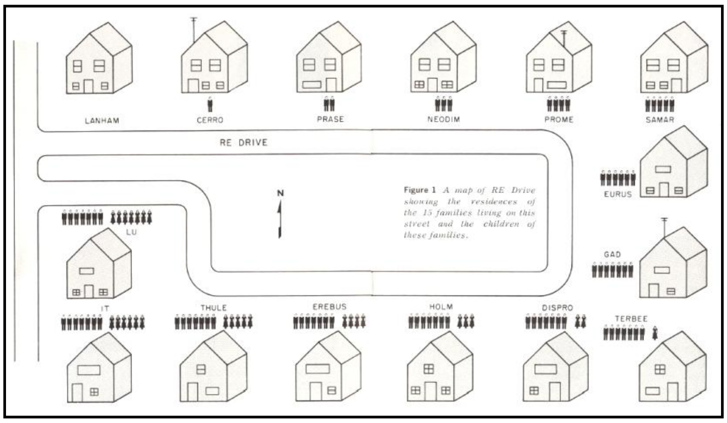


Figure 2 – "Rare Earth Drive"(Gschneidner Jr., 1964)

II. FLOTATION SURFACE CHEMISTRY FUNDAMENTALS

Froth flotation relies on the exploitation of variations in interfacial chemical properties of particles in solution. This is typically achieved via the adsorption of selective organic reagents (collectors, depressants, etc.) onto the desired mineral surfaces. To aid in understanding the adsorption phenomena occurring at the particle surfaces, we use fundamental surface chemistry techniques including zeta potential, adsorption density, and microflotation. In addition to increasing our understanding, these measurements allow for the prediction of the conditions needed to produce acceptable grades and recoveries in each respective process. The following subsections will provide a background on the fundamental surface chemistry techniques used in this research.

Electrical Double Layer Model

The adsorption of the collector at the mineral surface is largely controlled by the electrical nature of that mineral surface. To aid in the understanding of the electrical nature of particles in solution, the Electrical Double Layer Model is used. This model illustrates that the charge on the mineral surface is determined by the adsorption of potential determining ions onto the mineral. To maintain electro-neutrality, oppositely charged counter-ions firmly adsorb around the particle creating the Stern layer.

An example of this is shown in Figure 3 where a negatively charged particle is surrounded by a positively charged layer of ions known as the Stern layer. Other positively charged ions are still attracted to the negatively charged particle, but are repelled by the positively charged Stern Layer, as well as other positively charged ions present. This area is known as the Diffuse Layer or Gouy Layer. Positive ions in the diffuse layer have a high concentration near the surface, which gradually decreases with distance, until it reaches equilibrium with the counter-ion concentration of the bulk solution. The attached Stern layer and the charged Diffuse Layer make up the Double Layer Model.

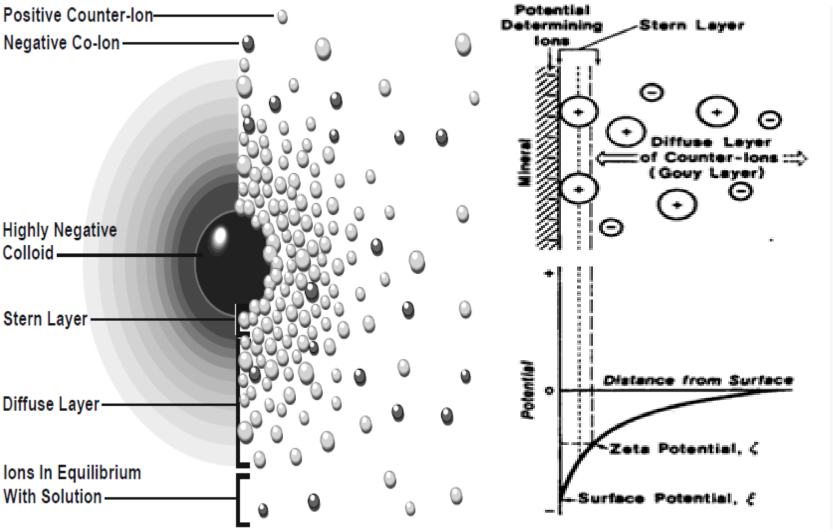


Figure 3 – Electrical Double Layer model of a negatively charged particle (Rao, 2004)

Zeta Potential

Formation of the double layer occurs to maintain electroneutrality of the system, and, in turn, causes a potential difference between the surface of the particle and any point within the solution. This potential difference is referred to as the surface potential and is on the order of millivolts. The charge of the particle and the thickness of the double layer are directly related to the magnitude of the surface potential. As the distance from the surface increases, the potential decreases as shown in Figure 4.

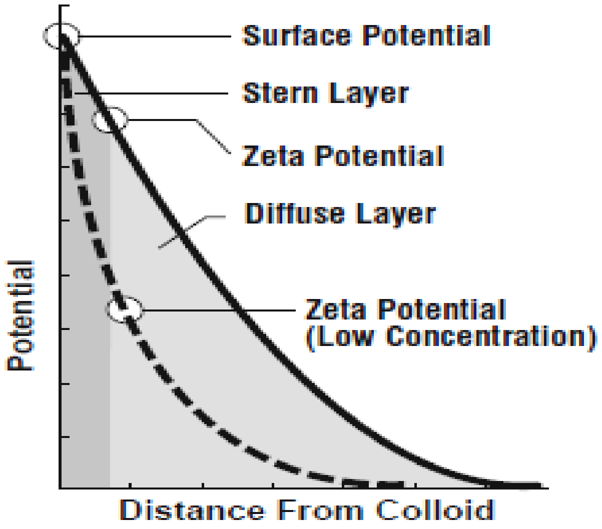


Figure 4– Potential as a function of distance from the particle (Ravina, 2013)

As a particle moves relative to the liquid, the Stern Layer moves along with the particle at the same velocity, while the Diffuse Layer shears away, creating a boundary known as the Slip Plane. The potential at this boundary is known as the Zeta Potential (ζ). Although, the magnitude of the zeta potential is less than the surface potential, it is considered more significant, since it typifies the actual interactions of charged particles in solution.

The pH at which the zeta potential equals zero is known as the Iso-Electric Point. At this point the electrokinetic charge density is also equal to zero. An example of the electrokinetic potential (zeta potential) of goethite (FeO(OH)) as a function of pH is illustrated in Figure 5. TheIEP of goethite occurs at approximately 7 on the pH scale. You will note that this value, IEP, does not vary as a function of sodium chloride molarity. In this case, sodium chloride is acting as what is known as an “indifferent electrolyte”, which effects the magnitude of the surface charge but does not shift the IEP. If the ions present in the electrolyte do alter the IEP, they are said to be “potential determining ions” or PDI’s. Upon further inspection of the figure, you can see that the researchers were using a physically adsorbing collector. This can be easily observed by looking at the recovery portion of the figure. In the pH region from 2 through 7, the zeta potential of goethite is positive. Thus, by using an anionic collector in this range, the recovery is high. Conversely, as the pH is increased (pH =7-12) the zeta potential decreases to negative values, by switching from anionic to cationic collectors, maximum recovery can be achieved. Understanding the zeta potential of the particles is fundamental in understanding how toobtain the most favorable operating conditions within the flotation system. It should be noted, that this situation typifies that of a physically adsorbing collector. In chemically adsorbing collectors,a chemical reaction takes place on the mineral surface, thus, these collectors are less sensitive to surface charge, that is, a anionic collector may still adsorb onto a negatively charged particle if there is a driving force for adsorption.

Adsorption Density

After determining the zeta potential of both the valuable and gangue minerals and proposing a reagent scheme for selective separation, it is necessary to understand the fundamentals of collector adsorption onto the desired mineral, i.e. physical or chemical adsorption. This is achieved through the use of thermodynamic models (adsorption isotherms) which represent a functional relationship between the amount of collector adsorbed on the mineral interface (µMol/g or µMol/cm^2) relative to its concentration (µMol) in the system at a constant temperature.

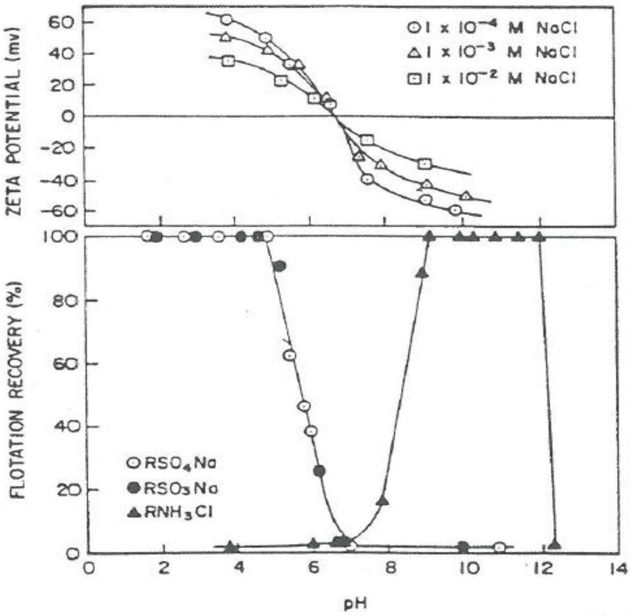


Figure 5– The effect of zeta potential on the IEP and recovery of goethite(Rao, 2004)

Data obtained from these models can be used to calculate the free energy, enthalpy, and entropy of adsorption values. These values can provide valuable insight into the nature of adsorption, including the effect of temperature.

In addition to providing a thermodynamic basis for the adsorption process, information obtained from adsorption density measurements provides insight into the formation of hemi-micelles on the mineral surface. Figure 6depicts the adsorption of an anionic collector adsorbing on a positively charged mineral surface. The far left of the figure shows a low collector concentration, the middle shows the formation of a hemi-micelle ("hemi" is Greek for half) on the mineral surface, and the far right illustrates "charge reversal" and formation of micelles.

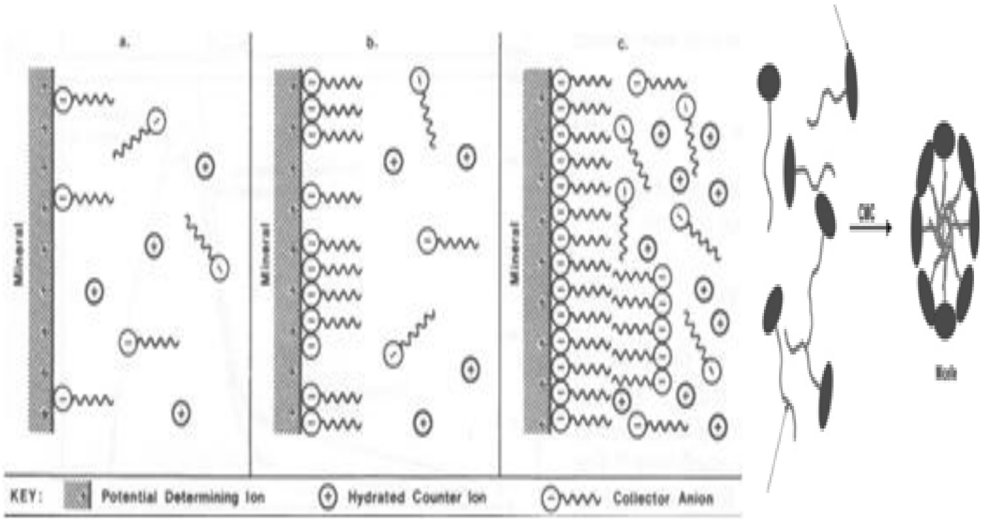


Figure 6– Effect of increasing the concentration of an anionic collector adsorbing on a positively charged mineral surface (Taylor, 2011)

The concentration at which no further adsorption occurs and micelles begin to form is known as the "critical micelle concentration". This phenomenon is illustrated by the plateau of various collectors adsorbing onto alumina, as shown in Figure 7(left). When the CMC is reached flotation performance can drastically decrease. Figure 7 (right) shows that the recovery of bastnasite decreases as the % collector adsorbed decreases.

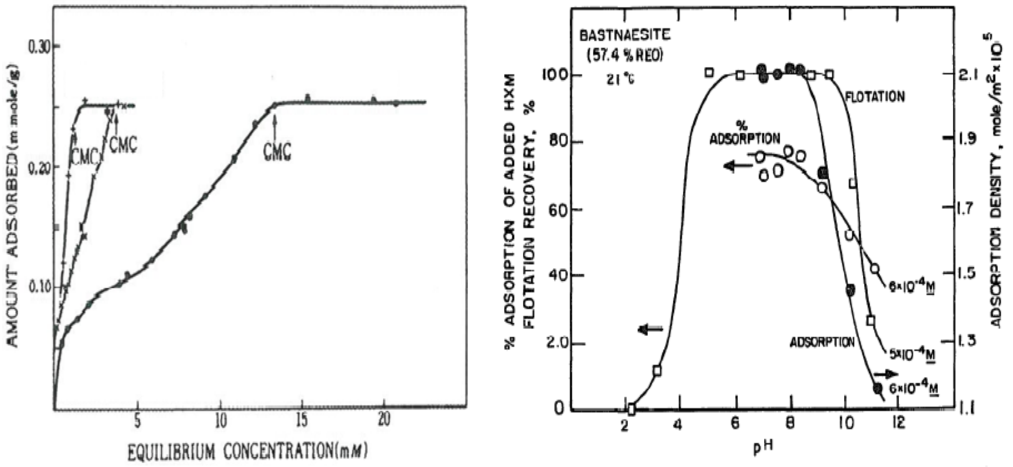


Figure 7– Adsorption of surfactants from aqueous solution by alumina: DAC, TAC, and HAC at 40°C (Rao, 2004) . (Right) correlation of adsorption density with flotation results of bastnasite (Pradip, 1981)

Rare Earth Flotation Review

Literature on the flotation of rare earth oxide minerals is a relatively limited. This is especially true with regard to fundamental flotation research, although, as the demand for rare earths continues to grow, the amount of research in the field is increasing rapidly.

The primary rare earth minerals are bastnasite (Ce,La(FCO$_3$)), monazite (Ce,La(PO$_4$)), and xenotime (YPO$_4$), and the primary gangue minerals are barite (BaSO$_4$) and calcite (CaCO$_3$). Ancylite ((RE)$_x$(Sr, Ca)$_{2-x}$(CO3)$_2$(OH)$_x$·(2-x)H$_2$O) has also been found as source of domestic rare earths (Cui 2015). Froth flotation relies on the separation of these minerals based on differences in their surface properties. Unfortunately, this is where the difficulty in rare earth flotation lies, i.e. both the desired and gangue minerals are oxides. Thus, efficient separation of one oxide from another can prove extremely complex. The following subsections will present both the past and present methodologies used commonly in rare earth flotation of bastnasite, monazite and xenotime.

Bastnasite Flotation

As the primary rare earth mineral at two of the world's largest rare earth mines (Mountain Pass, CA and Bayan Obo, China) bastnasite has been the main focus of rare earth flotation research for some time. During this time, a variety of collectors for the flotation of rare earths bastnasite have been investigated including: fatty acids, various hydroxamates, dicarboxylic acids, and phosphoric acids (Jordens et al. 2014).

Initially, the typical collector choice for REO flotation was fatty (carboxylic) acid due to the relatively low cost and high availability, but with recent advances in rare earth flotation research this trend may be changing. Unfortunately, fatty acid collectors are highly unselective on their own, and require large amounts of depressant addition to achieve the desired concentrate grades/recoveries. Some of the more commonly used gangue depressants include: sodium carbonate, lignin sulfonate, and sodium silicate. illustrates the studies performed on bastnasite in reverse chronological order, which are reviewed in the following paragraphs.

Table 1 – Fundamental Studies on Bastnasite Flotation

Author	Year	Mineral	Source	Test Type	IEP	pH Range Tested	pH of Max Recovery/ Adsorption	Collector	Depressant	Frother	Max Recovery
Jordens	2014	Bastnasite	Madagascar Mountain Pass, CA	Microflotation Zeta Potential	6.3 8.1	5-9	9.0	Benzohydroxamic Acid Phosphoric Acid Ester Sodium Oleate	Sodium Silicate	MIBC F150	95
Pradip/Fuerstenau	2013 1985, 1992 1981, 1983	Bastnasite Calcite Barite	Mountain Pass, CA Kansas South Carolina	Bench Scale Flotation Microflotation Zeta Potential Adsorption	9.5 Positive throughout range tested Positive throughout range tested	≈3-11	9.5	K-Octyl Hydroxamate Fatty Acid (Sodium Oleate)	Lignin Sulfonate	NA	≈95
Ren	2000	Bastnasite	China	Bench Scale Flotation Zeta Potential	7.8 (plain bastnasite) 8.1 (bastnasite w/ K Alum)	≈2-10	5.0	Benzoic Acid	Potassium Alum	NA	≈95
Pavez	1995	Bastnasite	Brazil	Microflotation	4.9	≈2-11	9.0	K-Octyl Hydroxamate Fatty Acid (Sodium Oleate)	NA	NA	≈95 ≈95
Ren	1997	Bastnasite	China	Bench Scale Flotation Microflotation Zeta Potential Adsorption	8.0 (plain) 5.9 (w/collector)	≈2-13	8.5-9.5	Modified Hydroxamic Acid	Sodium Sulfide	NA	≈95

Jordens et al. (2013) performed a study measuring the zeta potential of bastnasite in the presence of several different collectors (benzonhydroxamic acid, sodium oleate, and phosphoric acid ester). The isoelectric point of bastnasite was determined using electrophoretic (pH_{IEP}= 6.3) and electroacoustic (pH_{IEP} = 8.1) techniques. These results were then compared with results involving the microflotation of bastnasite and quartz. Results showed that both sodium oleate and the phosphoric acid ester were less selective for bastnasite flotation than the benzohydroxamic acid. Additionally, the researchers found that the recovery of bastnasite with benzohydroxamic acid is strongly dependent on the type of frother used, recovery was low with the weak frother Methyl Isobutyl Carbinol (MIBC) and high with strong frother Flottec F150 (proprietary mix of polygylcols) (Jordens et al., 2013).

Starting in the early 1980's, Pradip and Fuerstenau began their extensive studies on the flotation of bastnasite ore from Mountain Pass, CA (Pradip & Fuerstenau, 1981-2013). Their studies have primarily focused on the use of alkyl hydroxamates as an alternative to fatty acid collectors. In their most recent paper (Pradip & Fuerstenau 2013), they have shown that alkyl hydroxamates are capable of increased selectivity for bastnasite over gangue, and thus, an increase in concentrate grade. In addition to this, they have shown that it is possible to produce these higher grades at lower temperatures than are required when using fatty acids, which could prove beneficial by eliminating the need/cost involved in elevated temperature flotation. Thermodynamic calculations performed from their adsorption density measurements suggest that the adsorption of potassium-octyl hydroxamate follows an endothermic chemisorption mechanism (Pradip & Fuerstenau, 1985). They have also proposed that elevated temperature flotation increases the solubility of the collectors, as well as the minerals of interest. Since the proposed adsorption mechanism involves dissolution, hydrolysis, hydroxy complex formation, and re-adsorption or precipitation of this complex on the mineral surface, it is obvious that an increase in solubility of both the collector and mineral would aid in the adsorption process. Additionally, increasing the temperature increases the selectivity of hydroxamate for bastnasite by increasing the rate at which it adsorbs onto bastnasite relative to the gangue minerals present in the system.

Pavez and Peres (1994) performed zeta potential, adsorption, and microflotation experiments on both bastnasite and monazite, using octyl hydroxamate and sodium oleate as collectors. Their results agreed with Pradip and Jordens work, i.e. that the mechanism for both fatty acid and hydroxamate adsorption is chemisorption.

As alternative to “regular” hydroxamates, Ren et al. performed work on Chinese bastnasite using a modified hydroxamic acid (MOHA) as a collector. His experiments included the use of zeta potential, adsorption density, microflotation, and bench scale flotation. He proposed that the adsorption mechanism is also chemisorption via the formation of a chelation reaction between the MOHA and the trivalent cerium species present at the bastnasite mineral surface (Jun Ren et al., 1997). In addition to his work with pure bastnasite, Ren et al. investigated the use of various depressants to effectively separate bastnasite from monazite. He found that by using a small amount (0.3 g/L) of potassium alum, with benzoic acid as a collector, he could selectively float bastnasite from monazite. It was proposed that this was due to preferential adsorption of hydrolyzed aluminium ions onto the monazite mineral surface over bastnasite (Jun Ren et al., 2000).

The adsorption of anionic fatty acids onto rare earth mineral surfaces is postulated to be chemical in nature, as they adsorb onto the REO minerals at pH values where the mineral’s zeta potentials are negative(Jordens et al., 2013). Due to the unselective nature of fatty acid flotation, large amounts of depressants are needed to keep gangue minerals from floating. In addition to requiring large amounts of depressants, fatty acid flotation also requires elevated temperature for acceptable grades/recoveries. By elevating the temperature, the solubility and rate of adsorption/chemical reaction at the mineral surface is increased. The effect of temperature on both the grade and recovery of bastnasite flotation using a fatty acid collector are shown in Figure 8, where increasing the temperature from 18°C to 85°C greatly increases both the grade and recovery of rare earth oxides.

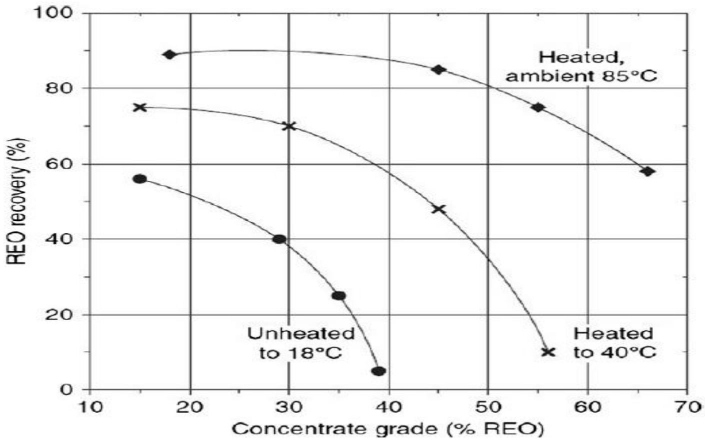


Figure 8– Effect of temperature on REO flotation using a fatty acid collector (Jordens et al., 2013)

Molycorp Flotation Process

Elevated temperature fatty acid flotation of bastnasite is the process currently used at Molycorp's Mountain Pass Mine and is shown in Figure 9. In their process, the bastnasite ore is crushed/ground/classified to a p80 of 325 US Mesh (45µm) prior to entering the flotation circuit. Upon entering the circuit the pulp is sent to four stages of elevated temperature (82°C) conditioning, these are as follows:

1) Soda ash (5 lbs/ton) is used to adjust the pH (Pradip, 1981). It also acts as a gangue (barite, calcite) depressant.
2) Blank stage to allow for further pH adjustment and depressing effect.
3) Lignin Sulfonate (5 lbs/ton) is added to depress gangue minerals present.
4) Fatty acid addition (0.14 lb/ton) is added as the collector.

After conditioning the pulp is sent to a 3 stage (2 cells/stage) rougher flotation circuit at 40% solids by weight. The rougher concentrate is sent to the cleaner conditioner, prior to four stages (multiple tanks/stage) of cleaning. This flowsheet produces a concentrate containing 60–70% REO with recoveries ranging from 60–70%. Thus, there may be significant room for improvement in the current flotation scheme used at Molycorp.

Recently, the use of chelating collectors, such as hydroxamates, has been receiving increased attention, due to their supposed increased selectivity for rare earths over fatty acids. The increase in selectivity is due to their ability to preferentially form chelates with rare earth ions over alkaline earth ions, that is, there is a thermodynamic driving force for the adsorption of hydroxamates onto rare earths rather than their associated gangue. An example of this thermodynamic driving force is illustrated in Table 2by the large stability constants for the formation of rare earth hydroxamates vs. the formation calcium hydroxamate.

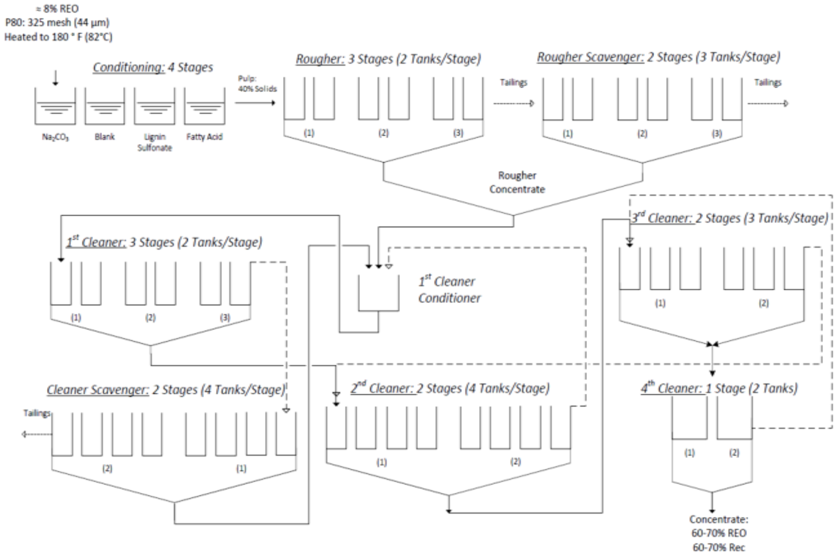
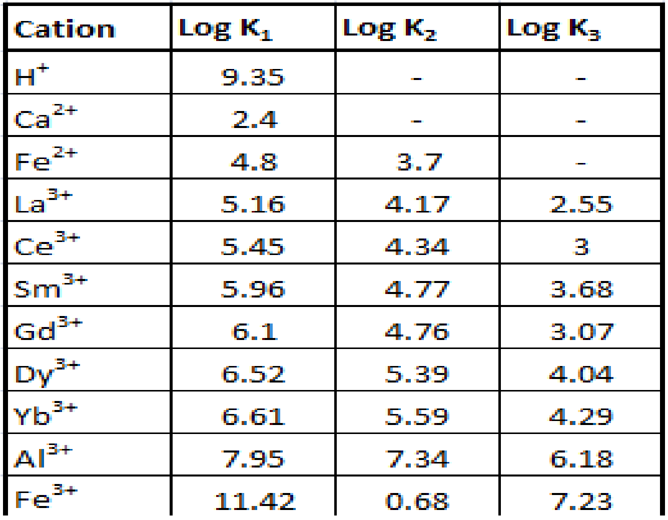


Figure 9–Molycorp flotation flowsheet 2014

Like fatty acids, the mechanism of hydroxamate adsorption is considered to be chemical in nature, as it adsorbs at a zeta potential where both the hydroxamate species and rare earth mineral are negative. Additionally, the adsorption of hydroxamate increases as a function of temperature, i.e. the free energy of adsorption becomes more negative as temperature increases. This is illustrated in Figure 10 where the free energy of adsorption of hydroxamate onto bastnasite is more negative than that of both calcite and barite, and becomes more negative as the temperature is increased.

Table 2– Stability Constants for Metal Hydroxamates (Pradip, 1981)



Cation	Log K_1	Log K_2	Log K_3
H^+	9.35	-	-
Ca^{2+}	2.4	-	-
Fe^{2+}	4.8	3.7	-
La^{3+}	5.16	4.17	2.55
Ce^{3+}	5.45	4.34	3
Sm^{3+}	5.96	4.77	3.68
Gd^{3+}	6.1	4.76	3.07
Dy^{3+}	6.52	5.39	4.04
Yb^{3+}	6.61	5.59	4.29
Al^{3+}	7.95	7.34	6.18
Fe^{3+}	11.42	0.68	7.23

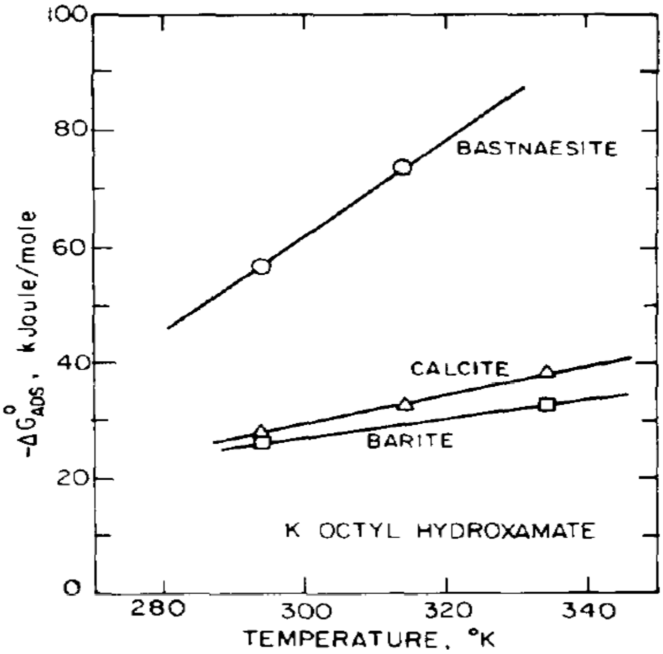


Figure 10– Stern-Grahame free energy of adsorption of potassium octyl hydroxamate on barite, calcite, and bastnasite as a function of temperature (Pradip & Fuerstenau, 1985)

Currently, the accepted mechanism for hydroxamate adsorption involves the dissolution of a metal to a cation, hydrolysis of this cation, formation of a hydroxy complex in solution, and finally the readsorption or precipitation of this complex onto the mineral surface (Pradip & Fuerstenau, 1985). This is shown below in Figure 11,where MOH^+ represents the hydrolyzed cation forming a chelation complex with neutral hydroxamic acid (top) or anionic hydroxamate (bottom).

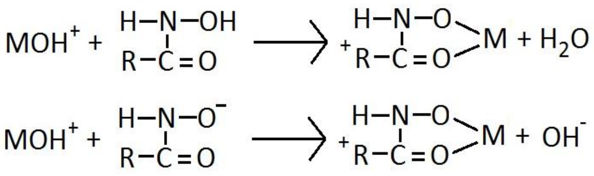


Figure 11– Schematic of chelation reaction between hydrolyzed cation and hydroxamic acid (top) or anionic hydroxamate (bottom) (Pradip, 1981)

Thus, for the successful application of hydroxamate as a collector, the mineral must be somewhat soluble, but, must also form a relatively insoluble hydroxamate complex for re-adsorption onto the mineral surface. Knowing the rare earth minerals are of semi-soluble nature, and form stable hydroxamate complexes, make them ideal for flotation with hydroxamates.

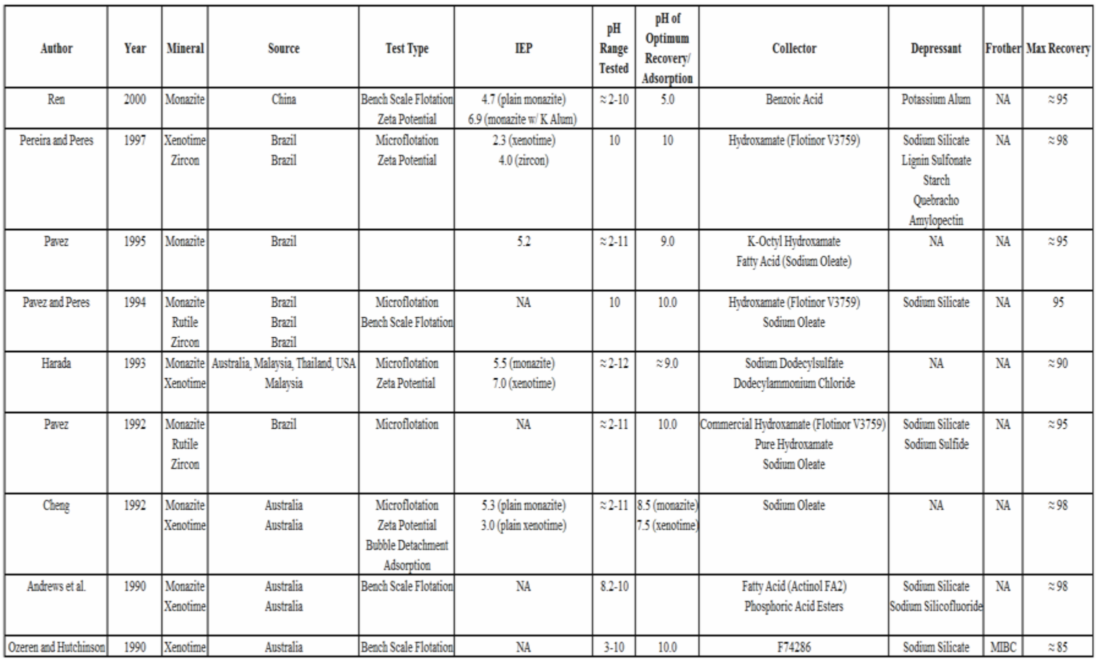
In addition to fatty acids and hydroxamates, phosphoric acid esters have also been investigated for use in rare earth flotation. Like the former collectors, these are primarily anionic in nature and are also thought to chemically adsorb on the mineral surface via a complexation reaction. Their lack of use is attributed to the acidic pH values required for adequate REO grades/recoveries to be obtained (Jordens et al., 2013).

Monazite/Xenotime Flotation

Monazite ((Ce,La)PO_4) and xenotime (YPO_4) are typically found together in deposits, with the amount of xenotime being approximately 0.5-5.0% of the monazite present. Monazite/xenotime can be in associated with bastnasite (e.g. Molycorp) or as the primary REO mineral in heavy mineral sands. When present in heavy mineral sands, the mineralogy of the deposit differs greatly to that of a bastnasite carbonatite type deposit. Gangue minerals in heavy mineral sand deposits may include ilmenite, rutile, zircon, and quartz. The monazite/xenotime surfaces seem to react similarly to both fatty acid and hydroxamate collectors, due to the presence of similar surface cations found in bastnasite (Ce,La,etc.) (Jordens et al., 2013). Unfortunately, the variation in gangue minerals present requires the use of different reagent schemes to achieve desirable separations. The majority of the schemes involve the same fatty acid collector/hydroxamate collector in combination with a depressant specific to the gangue mineral. Typical depressants include lignin sulfonate, sodium metasilicate, starch, quebracho, amylopectin(Pereira and Peres, 1997). Table 3 illustrates the studies performed on monazite and xenotime in reverse chronological order, which are reviewed in the following paragraphs.

Fundamental research on monazite varies widely, as the “ore” sources are quite unique. One of the more interesting xenotime sources comes from the non-conducting fraction of an electrostatically separated concentrate, containing 95% xenotime and 5% zircon. As an alternative to other physical concentration methods, Pereira and Peres performed zeta potential and microflotation tests in an effort to separate the xenotime from zircon. The collector used was a commercially supplied hydroxamate (Flotinor V3579), in conjunction with the use of lignin sulfonate, sodium metasilicate, starch, quebracho, and amylopectin as zircon depressants. Results indicated it was possible to recover approximately 95% of the xenotime, while effectively depressing the zircon using sodium silicate (Pereira & Peres, 1997).

Table 3 – Fundamental Studies on Monazite/Xenotime



Author	Year	Mineral	Source	Test Type	IEP	pH Range Tested	pH of Optimum Recovery/ Adsorption	Collector	Depressant	Frother	Max Recovery
Ren	2000	Monazite	China	Bench Scale Flotation Zeta Potential	4.7 (plain monazite) 6.9 (monazite w/ K Alum)	≈ 2-10	5.0	Benzoic Acid	Potassium Alum	NA	≈ 95
Pereira and Peres	1997	Xenotime Zircon	Brazil Brazil	Microflotation Zeta Potential	2.3 (xenotime) 4.0 (zircon)	10	10	Hydroxamate (Flotinor V3759)	Sodium Silicate Lignin Sulfonate Starch Quebracho Amylopectin	NA	≈ 98
Pavez	1995	Monazite	Brazil		5.2	≈ 2-11	9.0	K-Octyl Hydroxamate Fatty Acid (Sodium Oleate)	NA	NA	≈ 95
Pavez and Peres	1994	Monazite Rutile Zircon	Brazil Brazil Brazil	Microflotation Bench Scale Flotation	NA	10	10.0	Hydroxamate (Flotinor V3759) Sodium Oleate	Sodium Silicate	NA	95
Harada	1993	Monazite Xenotime	Australia, Malaysia, Thailand, USA Malaysia	Microflotation Zeta Potential	5.5 (monazite) 7.0 (xenotime)	≈ 2-12	≈ 9.0	Sodium Dodecylsulfate Dodecylammonium Chloride	NA	NA	≈ 90
Pavez	1992	Monazite Rutile Zircon	Brazil	Microflotation	NA	≈ 2-11	10.0	Commercial Hydroxamate (Flotinor V3759) Pure Hydroxamate Sodium Oleate	Sodium Silicate Sodium Sulfide	NA	≈ 95
Cheng	1992	Monazite Xenotime	Australia Australia	Microflotation Zeta Potential Bubble Detachment Adsorption	5.3 (plain monazite) 3.0 (plain xenotime)	≈ 2-11	8.5 (monazite) 7.5 (xenotime)	Sodium Oleate	NA	NA	≈ 98
Andrews et al.	1990	Monazite Xenotime	Australia Australia	Bench Scale Flotation	NA	8.2-10		Fatty Acid (Actinol FA2) Phosphoric Acid Esters	Sodium Silicate Sodium Silicofluoride	NA	≈ 98
Ozeren and Hutchinson	1990	Xenotime	Australia	Bench Scale Flotation	NA	3-10	10.0	F74286	Sodium Silicate	MIBC	≈ 85

Further work on the depression of zircon from monazite ores was performed using sodium silicate and sodium sulphide with both hydroxamate and sodium oleate as collectors. In their study, they performed micro and bench scale flotation on a Brazilian monazite ore(Pavez & Peres, 1993). Tests were performed using either hydroxamate or sodium oleate (fatty acid) as the collector in the presence of sodium metasilicate or sodium sulfide. They showed that a hydroxamate collector has the capability to increase rougher concentrate grade due to increased selectivity, but sodium oleate provided greater overall grade and recovery. Additionally, results indicated that by increasing the temperature, the depression of rutile and zircon increased(Pavez & Peres, 1993).

As an alternative to the use of fatty acids or hydroxamates, Harada et al. (Owada, 1993) performed a study on the flotation of monazite from xenotime using sodium dodecylsulfonate and dodecylammonium chloride as collectors. Results indicate these collectors may work to separate monazite from xenotime, with monazite grades approaching 85% and recoveries of 67%, using microflotation. Clearly, further bench-scale work needs to be performed to substantiate these results.

Paves and Peres (1994) performed micro and bench scale flotation on Brazilian monazite ore using the both sodium oleate and hydroxamate as collectors. Sodium metasilicate was used as the depressant. Results indicate that hydroxamates increase the concentrate grade due to higher selectivity, but oleate allows for higher recoveries to be achieved.

Cheng et al. used sodium oleate as a collector for Australian monazite and xenotime. His work included the use of zeta potential, microflotation, adsorption, and bubble detachment techniques. Results indicate that the adsorption of anionic sodium oleate is chemical in nature, as maximum floatability occurred at negative zeta potential (Cheng et al. 1993, 1994, 2000).

In addition to testing fatty acids and hydroxamates, phosphoric acid esters have also been tested in the flotation of monazite/xenotime. Andrews et al.(Andrews et al., 1990)performed bench scale flotation on Australian heavy mineral sands containing monazite and xenotime, using traditional fatty acids as well as phosphoric acid esters as collectors. Bench scale flotation results indicate that the phosphoric acid esters were more selective (higher grade), but fatty acids achieved the highest recoveries.

Current Flotation Studies

Finally,some recently completed flotation based beneficiation research thesis studies on ancylite, bastanasite, monazite and xenotime bearing rare earth minerals are now being finalized and published subject to confidentiality constraints. (Anderson 2015, Cui 2015, Cui & Anderson 2016a, 2016b, 2016b, Everly, 2017, Mushidi 2016, Mushidi& Anderson 2016, Schriner 2016, Schriner& Anderson2015, Zhang 2016, Zhang & Anderson, 2016a, 2016b).

III. SUMMARY

With the increased demand for rare earth end products such as catalysts, batteries, and permanent magnets, understanding the fundamentals behind rare earth separation processes, such as flotation, is paramount to maximizing operational efficiency. This paper has outlined these fundamentals, past and present rare earth flotation research, and its application to rare earth processing.

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