



Beneficiation of the Nechalacho rare earth deposit: Flotation response using benzohydroxamic acid[☆]



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ABSTRACT

Rare earth minerals (REM) may be beneficiated using a variety of separation techniques with froth flotation being the most commonly applied in operating REM separation plants. Many different collectors have been tested with traditional REM such as bastnäsite. The most successful are the hydroxamic acids. The Nechalacho deposit contains many REM for which there is minimal processing information in literature. Thus, experimental investigation into their flotation behaviour is required.

This work focuses on understanding the effect of a benzohydroxamic acid collector on the flotation of a REM enriched pre-concentrate from the Nechalacho deposit (after lab-scale gravity and magnetic separation steps). The lab-scale flotation response of the REM is quantified using mass recoveries, water recoveries, QEMSCAN and chemical assay data and TOF-SIMS in order to study the recovery, entrainment and kinetics of different REM. Three different flotation schemes are investigated to determine the effect of a secondary addition of collector as well as the addition of lead ions, a known activator in hydroxamic acid flotation. It is important to note that the goal of this work is to determine fundamental flotation properties of the different REM in the Nechalacho deposit. As such, the process investigated here is not indicative in any way of the current process design for this deposit.

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1. Introduction

1.1. Rare earth flotation

Rare earth elements (REE) include the lanthanoid series of elements as well as yttrium (in this work Sc was excluded). The demand for REE has been generally increasing over recent years, prompting the development of new REE sources (Binnemans et al., 2013). Many new primary sources of REE have been discovered and delineated, however the beneficiation of REE-bearing minerals (REM) requires significant additional research. Froth flotation is the most well-established separation technique for REM. However, it has only been applied using selected anionic reagents for the main REM (bastnäsite, monazite and xenotime) found in current deposits. There is a pressing need for research investigating the fundamental flotation characteristics of different REM to optimize process designs for developing REE deposits such as the Nechalacho deposit (Avalon Advanced Materials Inc.,

Canada). The literature on REM flotation has been thoroughly reviewed in Jordens et al. (2013) followed by surface chemistry investigations of selected individual minerals from the Nechalacho deposit (Jordens et al., 2014a,b; Malas et al., 2013). This work aims to build on this prior work with an investigation of the flotation characteristics of the Nechalacho deposit using a highly selective benzohydroxamic acid collector.

1.2. Flotation kinetics

The recovery of a given mineral in flotation as a function of time is often described by the first order flotation rate equation (Arbiter, 1985):

$$R = R_{max}(1 - e^{-kt}) \quad (1)$$

where t is flotation time (min), k is the flotation rate constant (min^{-1}) and R_{max} is the maximum recovery achievable at $t = \infty$. Comparison of flotation rate constants for different minerals is commonly used as a predictor for the possibility of a separation of two floatable components based on the kinetic rate of flotation recovery. An alternative method is to employ the modified flotation rate constant as proposed by Xu (1998):

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$$K_m = R_{max} \times k \quad (2)$$

where K_m is the modified flotation rate constant. Since it accounts for both the maximum recovery and the rate of recovery, it is more reflective of true selectivity in a flotation system. Thus, a selectivity index (Eq. (3)) can be defined by dividing the modified flotation rate constants of different minerals to give an indication of the possibility of separation of the two minerals in a multiple stage flotation process.

$$SI = \frac{K_{m1}}{K_{m2}} \quad (3)$$

1.3. Activators for hydroxamic acid flotation

The successful use of hydroxamic acids for REM flotation has been shown to require several conditions such as: alkaline pH (near the pKa of the given hydroxamic acid), the presence of metal cations on the mineral surface which are able to form stable chelates with hydroxamic acids, and minerals with sufficient solubility to allow for hydroxamic acid adsorption (Assis et al., 1996; Fuerstenau, 2005). Unfortunately, many REM, currently under investigation for their potential as sources of REE, have lower REE contents than traditional REM such as bastnäsite (~72% REO), and have diminished solubility compared to REE-bearing carbonate minerals. A potential solution to these deficiencies is the use of activators to adsorb onto the REM surface and facilitate collector adsorption. One of the most common activators in flotation systems employing anionic collectors, such as hydroxamic acids, are polyvalent metal cations (Fuerstenau and Palmer, 1976). The most common example of this is the use of calcium ions to enhance the adsorption of sodium oleate onto quartz at alkaline pH (Fuerstenau and Palmer, 1976). In this situation the adsorption of calcium onto the quartz surface has been shown to only occur at a pH where the calcium is present in a monohydroxy state. This tendency for activation only when the metal cation is in a monohydroxy state, is observed with many other metal cations (Fuerstenau and Palmer, 1976). In the case of hydroxamic acid flotation, the metal cation used must also have a high metal-hydroxamate stability constant so that the collector will selectively adsorb to the metal cations used as activators. Previous works have used Fe ions to increase hydroxamic acid flotation of quartz, cassiterite and allanite (Herrera-Urbina and Fuerstenau, 1987; Jordens et al., 2014c; Sreenivas and Padmanabhan, 2002). While iron forms the most stable complexes with hydroxamic acids, it is difficult to maintain the correct oxidation state of the iron ions in solution at alkaline pH during flotation due to the oxidative nature of the flotation process. An alternative metal ion with correct speciation at alkaline pH and relatively high metal-hydroxamate stability constant is lead. This ion has been investigated previously with the Nechalacho deposit to improve REM flotation (Xia et al., 2015)

1.4. Paper objectives

The objective of this paper is to determine the flotation characteristics of the various REM present in the Nechalacho REE deposit through lab-scale flotation testing with a hydroxamate-based collector. Through the use of QEMSCAN, ICP-MS and the first-order flotation rate model, baseline flotation behaviours of the different REM are assessed. After the initial flotation recovery, three different reconditioning steps are investigated to determine the best approach for improving REM recoveries. It is important to note that the goal of this work is to determine fundamental flotation properties (e.g. impacts of surface modifications on flotation kinetics and absolute recoveries) of the different REM in the Nechalacho deposit. As such, the process investigated here is not indicative in any way of the current process design for this deposit.

2. Materials and methods

2.1. Material

The raw material used in this work originated from the Nechalacho REE deposit (Avalon Advanced Materials Inc., Canada) located in the Northwest Territories of Canada. Prior to flotation, the ore was subject to a series of gravity and magnetic pre-concentration steps as detailed in Jordens et al. (2016a,b). The highest grade product ($k_{50} = 50 \mu\text{m}$) from the gravity and magnetic separation was selected for downstream flotation experiments to determine the flotation behaviour of the different REM in the deposit. A high grade feed is important to this work as direct flotation of the ore would be much less likely to produce flotation concentrates with high enough grades of the minor REM to reliably assess their floatability (which may have a significant effect on the overall grade and recovery of REE). The mineralogy of the flotation feed may be seen in Table 1. Table 2 shows the average liberation, as determined from QEMSCAN, of selected minerals in the flotation feed. In this table “Free + Liberated” indicates any particle in which the mineral of interest covers >80% of the particle surface.

Reagents used in this work included benzohydroxamic acid (Alfa Aesar, USA), F150 (a polypropylene glycol-based frother obtained from Flottec, USA) and lead chloride (Fisher Scientific, USA). Sodium hydroxide and hydrochloric acid (Fisher Scientific, USA) were used for pH modification in all tests, diluted to 0.1–1 M. For each test fresh solutions of benzohydroxamic acid and lead chloride were prepared by dissolving the 1 g and 0.1 g, respectively, in approximately 150 mL of deionized water to form aqueous solutions.

2.2. Flotation

All flotation tests were carried out using a 1.2 L Denver lab-scale flotation cell operated at 1200 rpm with a constant air flow rate of

Table 1
Mineralogy of flotation feed (determined by QEMSCAN).

Mineral	Grade (wt.%)
Columbite(Fe)	1.06
Fergusonite	0.64
Bastnäsite	2.82
Synchysite	1.68
Allanite	1.66
Monazite	0.84
Zircon	35.25
Total REM	43.94
Quartz	11.82
Plagioclase	14.15
K-Feldspar	10.22
Fe-oxides	10.16
Other	9.70
Total gangue	56.06

Table 2
Liberation characteristics of selected minerals in the flotation feed.

Mineral	Free + liberated (%)
Zircon	83.5
Fe-oxides	62.9
Allanite	58.6
Bastnäsite/synchysite	54.4
Fergusonite	26.8
Columbite	34.7
Monazite	69.1

Table 3
Reagent additions at reconditioning stage.

Number	Label	Reconditioning stage
1	No Bz	No reagent addition
2	+Bz	5 kg/t benzohydroxamic acid
3	+Pb +Bz	0.5 kg/t PbCl ₂ + 5 kg/t benzohydroxamic acid

5.6 L/min. For each flotation test 200 g of the high grade feed was mixed with tap water in the cell, with the water level adjusted to the 1.2 L level line immediately prior to turning on the air. The suspension was allowed to condition for 1 min after the addition of collector (5 kg/ton benzohydroxamic acid) and pH adjustment. All flotation tests were carried out at an initial pH of 9 with 2 drops of F150 added to the cell. Concentrate collection was carried out for 5 min before reconditioning and 7 min after reconditioning. A total of 7 concentrates were collected at 0.5, 1, 2, 5, 5.5, 6 and 12 min cumulative time with the pulp level re-adjusted to approximately 1.2 L after each concentrate. The reconditioning stage consisted of 2 min of conditioning with different reagent additions depending on the test. For every test the pH was readjusted to 9 and a single drop of F150 was added during the reconditioning stage. The three different reconditioning stages investigated were: no further addition of collector, the addition of a further 5 kg/ton (relative to the initial feed mass) of benzohydroxamic acid, and the addition of 500 g/ton (relative to the initial feed mass) of PbCl₂ followed by a further 5 kg/ton of benzohydroxamic acid. In the case of the dual addition of lead and benzohydroxamic acid the suspension was allowed to condition for 1 min with the lead followed by 1 min with the benzohydroxamic acid. The lead chloride solution was adjusted to pH 9 prior to adding it to the cell. The three different reconditioning approaches are described in Table 3. Sufficient repeat tests were carried out to ensure repeatability and to produce sufficient mass for analysis of each concentrate obtained under each condition.

2.3. Quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN)

Concentrates and tailings from flotation experiments were prepared as polished sections and analysed by QEMSCAN at the Advanced Mineralogy Facility at SGS Canada (Lakefield, Canada). QEMSCAN analyses were performed on an EVO 430 automated scanning electron microscope equipped with four light-element energy-dispersive X-ray spectrometers and iDiscover software used to process the resultant data and images. The scanning electron microscope operates with a 25 kV accelerating voltage and 5 nA beam current. In this arrangement scanning electron microscope data is measured and processed from every pixel across a sample with the pixel size defined by the scope of the analysis. Each pixel is assigned a mineral name by the iDiscover software based on 1000 counts of energy dispersive X-ray spectral data and backscatter electron intensities. The Particle Mineral Analysis (PMA) method was used for all samples in this study. PMA is a two-dimensional mapping analysis used to resolve liberation and locking characteristics of a generic set of particles. A pre-defined number of particles were mapped at a 3–6 μm pixel size.

If the constituent phases in the sample are chemically distinct, the QEMSCAN technique is capable of reliably discriminating and quantifying minerals. Magnetite, hematite and other minor iron oxides are grouped together and referred to as Fe-oxides. Mineral definitions for this deposit were validated and refined to fit the particular samples. X-ray diffraction (to define major minerals), scanning electron microscopy and electron probe micro analysis were used to develop a reference mineral list. REM in QEMSCAN

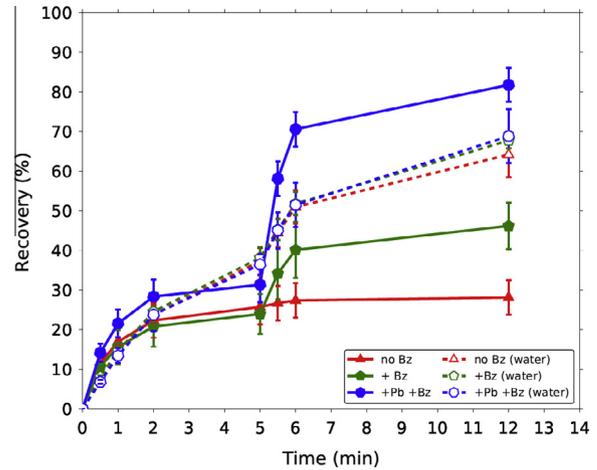


Fig. 1. Cumulative mass pull (polygons) versus time for the three different flotation conditions investigated including reconditioning without collector addition (no Bz), reconditioning with a secondary addition of collector (+Bz), and reconditioning with lead ions followed by a secondary addition of collector (+Pb +Bz). Also shown are water recoveries (unfilled polygons) for all three conditions. Error bars represent 95% confidence intervals.

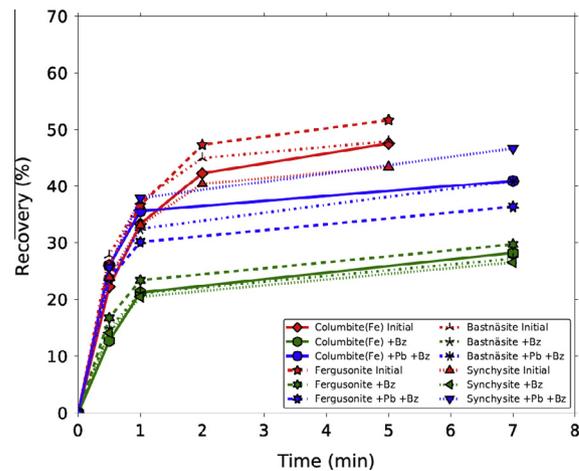


Fig. 2. Mineral recovery as a function of time for three different conditions (initial flotation recovery, recovery after reconditioning with additional benzohydroxamic acid, recovery after reconditioning with lead ions followed by additional benzohydroxamic acid). The four minerals presented here are columbite(Fe), fergusonite, bastnäsite and synchysite.

in this work were identified based on their REE composition. QEMSCAN will not measure the exact chemistry of the minerals, it merely selects the most suitable mineral phase based on the developed reference mineral list.

2.4. Inductively coupled plasma mass spectrometry

The REE, Fe, Zr, U and Th content of all samples was determined by inductively coupled plasma mass spectrometry (ICP-MS). As there are many difficulties in digesting silicate minerals from this deposit, 0.1 g of sample was mixed with sodium peroxide and then heated to produce a homogeneous melt which was subsequently digested in hydrochloric acid and then analysed. Digestions and ICP-MS analysis was conducted by SGS Canada (Lakefield, Canada). For data validation purposes, calculated assays from QEMSCAN measurements were compared to chemical assays obtained from ICP-MS.

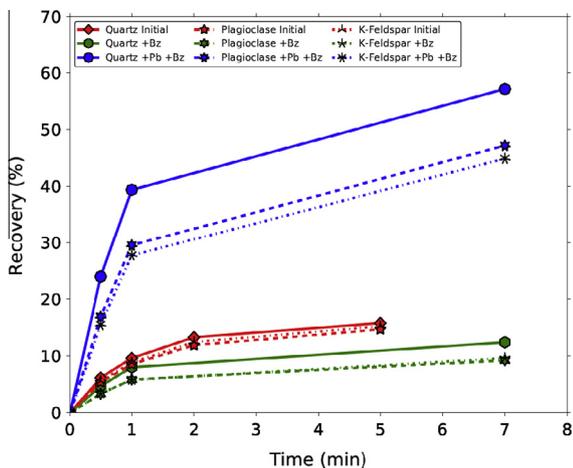


Fig. 3. Mineral recovery as a function of time for three different conditions (initial flotation recovery, recovery after reconditioning with additional benzohydroxamic acid, recovery after reconditioning with lead ions followed by additional benzohydroxamic acid) corresponding to thick solid lines, thin solid lines and dashed lines respectively. The three minerals presented here are quartz, plagioclase and K-feldspar.

2.5. Time of flight secondary ion mass spectrometry (TOF-SIMS)

Time of flight secondary ion mass spectrometry (TOF-SIMS) was used in this work to investigate changes in collector surface loading as well as the impact of lead ions added as a flotation activator. Samples were taken from the flotation pulp concentrates and tails, deoxygenated using bubbled nitrogen and then frozen in liquid nitrogen prior to analysis. Samples must be frozen immediately after collection in order to preserve their surface chemical characteristics.

Samples were analysed by first desliming a sub-sample in deionized water and then depositing the sub-sample onto a piece of indium foil. The indium foil was then placed into the instrument where it was degassed, thus minimizing any exposure to atmosphere. The reagent used in this work, benzohydroxamic acid, was analysed separately in order to identify characteristic peaks. All samples were prepared according to the method outlined by Smart et al. (2003). The instrument used in this work is an ION-TOF, ToF SIMS IV™ time of flight secondary ion mass spectrometer. This technique allows for the analysis of the outermost 1–3 atomic layers of a surface by mass spectrometry. An isotopically enriched $^{209}\text{Bi}^+$ (Bismuth) primary ion beam is rastered across an area of interest on the sample surface. The raster size used was $500 \times 500 \mu\text{m}$ with a total acquisition time of 100 s. The bombardment of the surface with the bismuth primary ion beam induces the emission of positively and negatively charged secondary ions from the sample surface. These secondary ions are extracted from the sample surface and mass analysed using a time-of-flight mass spectrometer. A plot of secondary ion intensity versus mass results in a traditional first order mass spectrum, with a resolution of 10,000 above 200 atomic mass units (amu). The Bi ion gun was operated at 25 kV Bi^{3+} with a current of $\sim 0.3 \text{ pA}$, pulsed at 1 ns with a beam spot size $\sim 1 \mu\text{m}$. All sample charging was neutralized with an electron flood gun.

3. Results and discussion

3.1. Mass recovery

The cumulative mass pull from the Nechalacho flotation tests as a function of concentrate collection time can be seen in Fig. 1. The

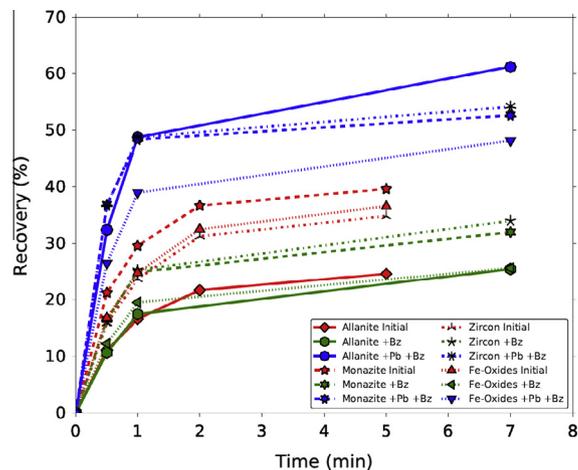


Fig. 4. Mineral recovery as a function of time for three different conditions (initial flotation recovery, recovery after reconditioning with additional benzohydroxamic acid, recovery after reconditioning with lead ions followed by additional benzohydroxamic acid) corresponding to thick solid lines, thin solid lines and dashed lines respectively. The four minerals presented here are allanite, monazite, zircon and Fe-oxides.

results indicate that the changes in reagent addition after reconditioning produced pronounced differences in mass recovery. Without additional reagent addition, the bulk of the mass recovery occurs over the first 2 min of flotation, indicating the kinetics of flotation are quite rapid with this collector (benzohydroxamic acid). After reconditioning, the baseline condition (no further reagent addition) shows little additional mass recovery. In contrast, the secondary addition of collector shows a significant increase in mass recovery, with the bulk of the mass recovered in the first 1 min of collection after reconditioning. The third condition with both Pb and benzohydroxamic acid additions at the reconditioning stage produces an even more significant increase in mass recovery, with the bulk of this recovery again occurring within the first 1 min of concentrate collection.

3.2. Water recovery

The cumulative water recoveries associated with the three flotation conditions are shown in Fig. 1. It can be concluded from this figure that there is little difference in water recovery between flotation conditions. The relatively high levels of water recovery are a result of the repeated adjustment of pulp level after each concentrate collection by adding additional water. It can also be inferred from Fig. 1, based on the well-established correlation of fine particle entrainment with water recovery shown by Trahar (1981) and others, that the observed differences in mass recovery in Fig. 1 are not due simply to an increase in non-selective entrainment.

3.3. Mineral recovery

In order to compare the differences between reconditioning steps, the concentrates produced after reconditioning are considered as distinct products from the initial flotation stage. The recoveries for post-reconditioning concentrates are calculated as a percentage of the initial flotation feed but are not considered cumulative with the initial 5 min collection time. The recoveries versus time for different minerals in the flotation feed may be seen in Figs. 2–4 for all REM as well as the major gangue minerals (Table 1). The conditions include the initial flotation over a 5 min period as well as the 7 min collection after reconditioning with additional benzohydroxamic acid, and lead ions. The recoveries

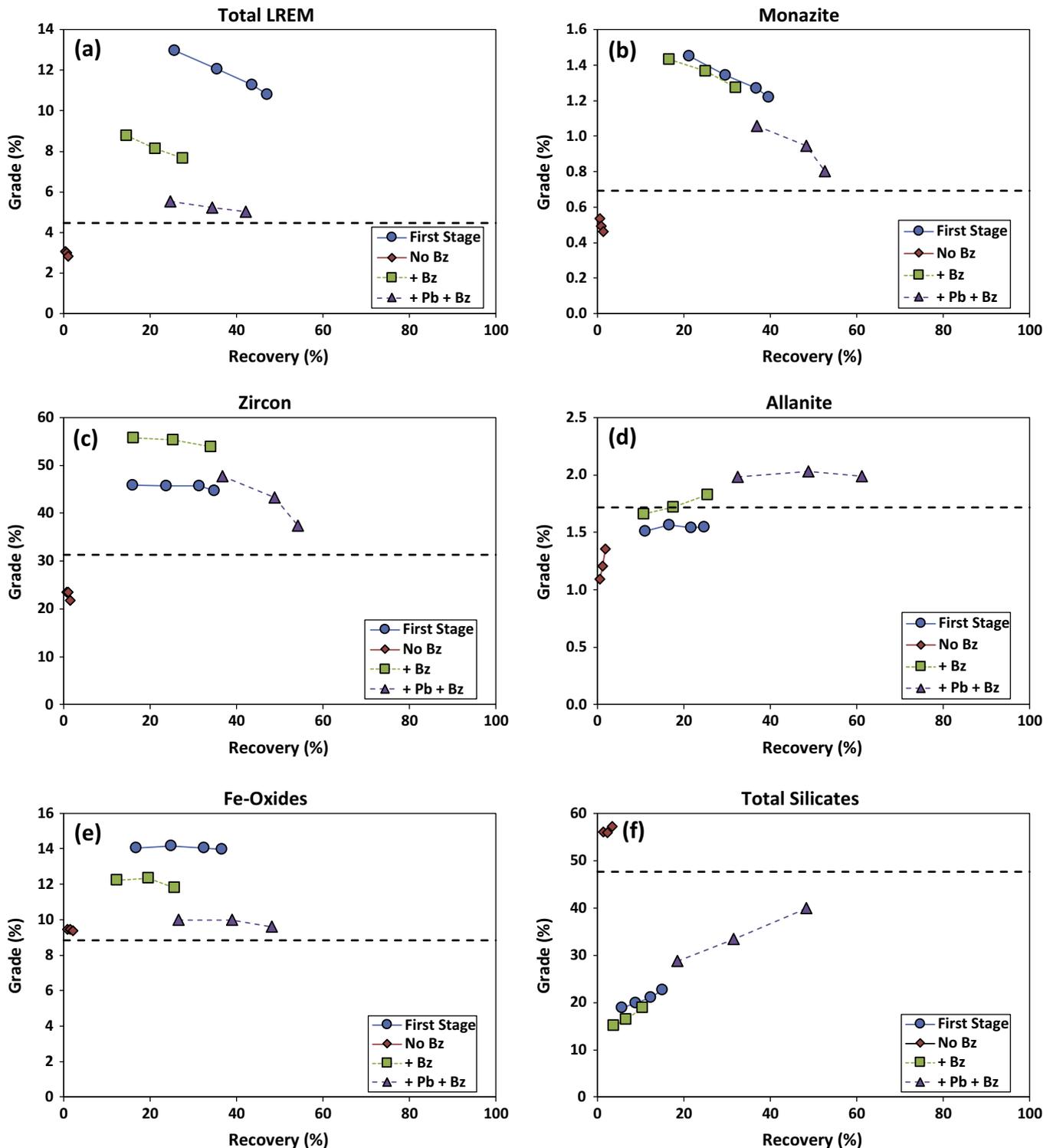


Fig. 5. Cumulative grade and recovery of flotation concentrates produced before reconditioning and after reconditioning. In the cases of flotation concentrates produced after reconditioning they have been treated as distinct from the initial flotation stage and are therefore not cumulative with the initial flotation stages. Minerals represented here include: (a) LREM (columbite, fergusonite, bastnäsite and synchysite), (b) monazite, (c) zircon, (d) allanite, (e) iron oxides and (f) silicates (quartz and feldspars). Dashed horizontal lines represent feed grades.

of four REM (bastnäsite, synchysite, fergusonite and columbite) are shown in Fig. 2 grouped together due to their observed similar flotation response. Similarly, the major silicate gangue minerals (quartz, plagioclase and K-feldspar) are shown in Fig. 3. These two groups of minerals respond similarly regardless of flotation conditions. Whether this observed similarity is due to true flota-

tion behaviour or mineral association, the two groups are treated as single phases (light REM and silicates, respectively) in order to simplify further analysis. The remaining major constituents of the flotation feed (allanite, monazite, zircon and iron oxides) are shown in Fig. 4. These four minerals do not show any obvious correlations, and thus are treated individually in subsequent sections.

Table 4

Output of non-linear regression fitting to first-order flotation rate equation for major minerals from the Nechalacho deposit along with mineral type and selected chemical composition information (from QEMSCAN mineral definition database) for each mineral. Minerals sorted by modified flotation rate constant (bolded).

Mineral	Type	R _{max} (%)	k (min ⁻¹)	k _M	REE (%)	Fe (%)	Nb (%)	Zr (%)	Total (%)
Bastnäsite	Carbonate	47.2	1.7	79.0	63.6	0.1	–	–	63.7
Fergusonite	Niobate	51.3	1.3	67.9	40.0	0.7	32.2	–	72.9
Synchysite	Carbonate	42.9	1.5	66.4	46.5–63.6	0.10	–	–	55.1
Columbite(Fe)	Niobate	47.2	1.2	58.0	0.4	14.8	49.4	–	64.6
Monazite	Phosphate	39.2	1.5	57.8	59.1	0.1	–	–	59.2
Fe-oxides	Oxide	36.4	1.2	42.7	–	70.0–77.7	–	–	73.9
Zircon	Silicate	34.8	1.2	40.7	2.3	0.9	0.4	44.8	48.4
Allanite	Silicate	24.5	1.2	28.2	22.6	11.1	–	–	33.7
Quartz	Silicate	15.9	0.9	14.9	–	–	–	–	0.00
Feldspar	Silicate	15.0	0.9	12.9	–	–	–	–	0.00

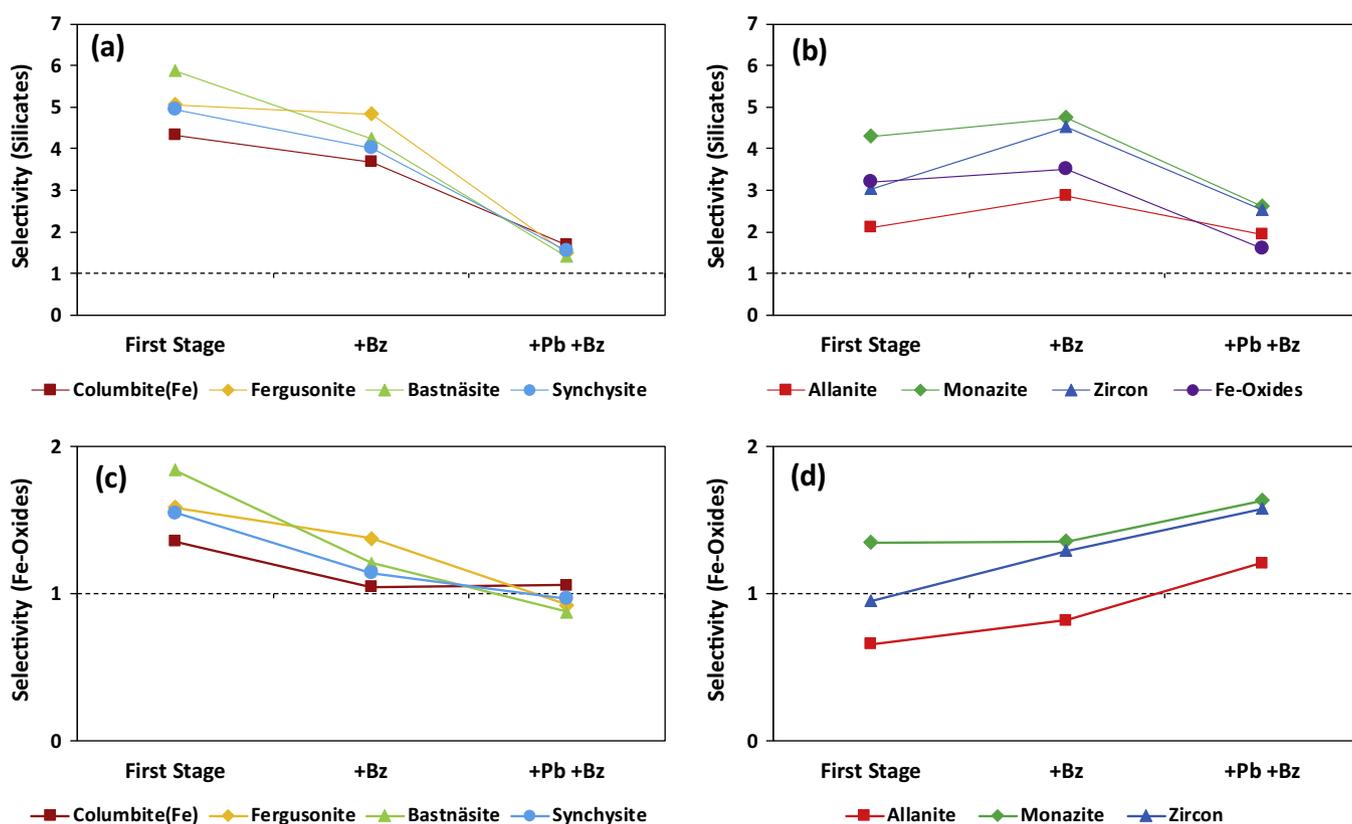


Fig. 6. Comparison of selectivity index for columbite, fergusonite, bastnäsite and synchysite (a, c) and allanite, monazite and zircon (b, d) relative to silicates (a, b) and iron oxides (c, d). The selectivity of iron oxides over silicates is shown in b). The selectivities of these minerals are compared between the initial flotation condition, the flotation after reconditioning with additional collector (+Bz) and flotation after reconditioning with lead and collector (+Pb +Bz).

A comparison of the different flotation conditions in Fig. 2 shows that the initial flotation recovery prior to reconditioning functions very well at collecting this group of light REE-bearing minerals. The addition of further collector in Fig. 3 has little effect on the collection of silicate gangue minerals. However, the presence of lead prior to further collector addition significantly increases the recovery of these gangue minerals (especially quartz). The results in Fig. 3 also indicate that quartz recovery is more sensitive to the addition of lead than feldspar recovery. A similar effect is illustrated in Fig. 4 where the addition of lead increases the recovery of allanite, monazite, zircon and iron oxides. Allanite in particular exhibits an increase of approximately 40% due to the addition of lead.

These results agree with a previous investigation by Xia et al. (2015) into the use of lead and hydroxamic acid for the flotation of this deposit. In the previous work, flotation with lead was found to preferentially increase the recovery of REE along with silicate

minerals (Xia et al., 2015). The selectivity of lead for quartz over feldspar is also confirmed in this work by the observation of an increased concentration of Si surface ions in the flotation concentrate without a corresponding increase in Na, K or Al ions present in feldspar minerals (Xia et al., 2015). However, the results in this study do not completely agree with the work of Xia et al. (2015). Key differences between the two studies include the use of: a lab-scale Denver flotation cell rather than microflotation, a pre-concentrated REM feed rather than direct ore flotation, PbCl₂ instead of Pb(NO₃)₂, different hydroxamic acid collectors, different collector dosages, and the lack of depressant or heated flotation pulps (approximately 45–55 °C) in this work.

3.4. Grade-recovery comparison

While the increased recovery of REM due to the addition of collector (and lead) during the reconditioning stages of flotation

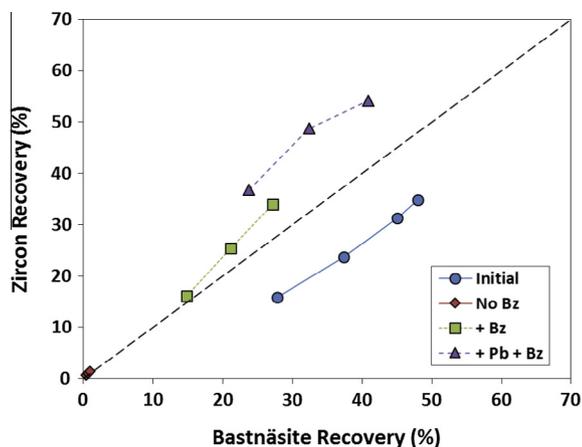


Fig. 7. Selectivity of zircon versus bastnäsite for different flotation conditions including initial flotation with benzohydroxamic acid, flotation after reconditioning with additional collector (+Bz) and flotation after reconditioning with lead and collector (+Pb +Bz).

is illustrated by Figs. 2–4, it is important to also consider the grade of these flotation concentrates. The ultimate goal of any REM beneficiation process for this deposit is to recover as much of the value REE as possible, while simultaneously minimizing the presence of gangue minerals with significant processing costs (i.e. silicates and iron oxides) in downstream metallurgical processes. The grade-recovery relationships for various minerals in this deposit are shown in Fig. 5 for both the initial flotation concentrates collected prior to reconditioning and all three sets of flotation concentrates collected after reconditioning.

Fig. 5a and e illustrate that the initial flotation conditions (addition of 5 kg/ton benzohydroxamic acid and flotation for 5 min) produce the best grade and recovery for both LREM and iron oxide minerals. This may indicate the preference of benzohydroxamic acid for these minerals, which is problematic as iron oxides are a deleterious gangue mineral in this deposit. Conversely, the addition of benzohydroxamic acid (in combination with lead) at the reconditioning stage produces significantly better results for allanite, zircon and to some extent monazite (Fig. 5b–d). The poor flotation of allanite without the addition of lead to act as an activator has been confirmed with this reagent in single mineral microflotation and surface chemistry studies (Jordens et al., 2014a). Potential explanations for this include a lack of sufficient REE cations on the allanite surface or differences in mineral structure and solubility relative to more traditional REM, for which hydroxamic acids are very successful collectors, such as bastnäsite. The grade and recovery for silicates indicates that prolonged flotation times result in an increase in silicate grade and recovery for all flotation conditions (Fig. 5f). The addition of lead ions in particular, causes a significant increase in silicate recovery.

3.5. REM kinetics

In order to understand the flotation behaviour of the various minerals on a relative basis the initial (i.e. first 5 min) recovery data as a function of time was fitted to the first order flotation rate equation, as discussed in Section 1.2, using the statistical software Stata13 (StataCorp, USA) to perform non-linear regressions. The outputs of these regressions (maximum recovery, flotation rate constant, and modified flotation rate constant) and the major metal cation composition information for the given minerals are shown in Table 4. The minerals are sorted by decreasing modified flotation rate constant. Bastnäsite shows the highest flotation rate and feldspar the lowest. The data indicate a clear differentiation of flotation kinetic behaviour according to mineral type. Carbonates and niobates show the highest flotation rates and silicates the lowest. This trend may be due to the effect of differences in mineral solubility on hydroxamate flotation as proposed by Assis et al. (1996) with carbonates expected to have a much higher degree of solubility than silicates. Another identifiable trend is the decrease in flotation associated with a decrease in metal cations on which benzohydroxamic acid is likely to preferentially adsorb. Hydroxamic acids in general will prefer the formation of stable chelates with REE, Fe and to some extent Nb and Zr over Na, K or Si (Fuerstenau, 2005; Gibson et al., 2015; Pavez and Peres, 1993).

Similar regressions were also completed for the flotation recoveries after different reconditioning stages. Using the fitted parameters from these non-linear regressions the selectivity index, a ratio of modified rate constants as discussed in Section 1.2, of each mineral relative to the major gangue minerals (silicates and iron oxides) was calculated. A comparison of the selectivity indices (Eq. (3)) between different conditions is shown in Fig. 6. Fig. 6a and c indicates that the most selective flotation condition for the LREM (fergusonite, columbite, bastnäsite and synchysite) is the initial flotation stage with only benzohydroxamic acid. Conversely, the flotation of allanite, zircon and monazite has increased selectivity relative to silicates (Fig. 6b) after reconditioning with benzohydroxamic acid. The flotation of iron oxides is a special case where these minerals are floated preferentially (relative to silicates) with benzohydroxamic acid collector (Fig. 6b). However, the addition of lead ions appears to slightly improve the selectivity of allanite, zircon and monazite relative to iron oxide minerals (Fig. 6d).

A more traditional representation of the selectivity of different flotation conditions for zircon (the major heavy REM) versus bastnäsite (a major light REM) is shown in Fig. 7. Based on this figure and the preceding kinetic information it seems likely that staged additions of benzohydroxamic acid could be beneficial to the flotation of this deposit due to the different floatabilities of the various REMs and the rapid kinetics of flotation with benzohydroxamic acid in general.

The use of total mineral recoveries for flotation kinetic modelling is a very common method however, these total recovery numbers may mask the impact of mineral associations, especially

Table 5
Output of non-linear regression fitting to first-order flotation rate equation for “free” REM particles along with mineral type and selected chemical composition information (from QEMSCAN mineral definition database) for each mineral. Minerals sorted by modified flotation rate constant (bolded).

Mineral	Type	R_{max} (%)	k (min ⁻¹)	k_M	REE + Fe + Nb (%)
Fergusonite	Niobate	85.6	1.7	144.3	72.9
Bastnäsite/synchysite	Carbonate	66.7	1.8	118.6	55.1
Columbite(Fe)	Niobate	73.1	1.2	88.1	64.6
Monazite	Phosphate	44.7	1.5	65.4	59.2
Fe-Oxides	Oxide	47.8	1.2	56.8	73.9
Zircon	Silicate	39.2	1.2	45.1	48.4
Allanite	Silicate	32.8	1.2	40.2	33.7

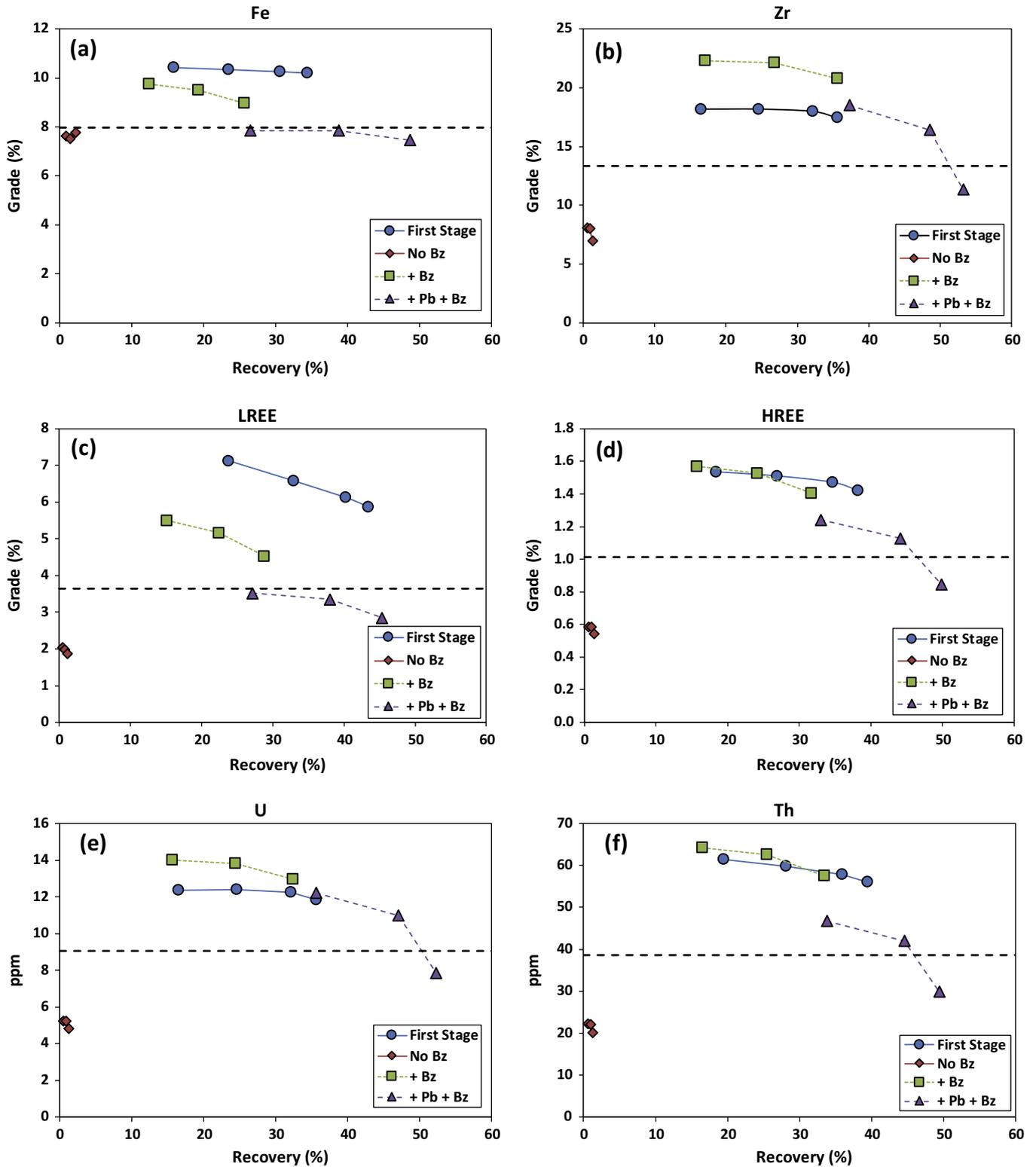


Fig. 8. Cumulative elemental grade and recovery of flotation concentrates produced before reconditioning and after reconditioning. In the cases of flotation concentrates produced after reconditioning they have been treated as distinct from the initial flotation stage and are therefore not cumulative with the initial flotation stages. Elements represented here include: (a) iron, (b) zirconium, (c) light REE, (d) heavy REE, (e) uranium, (f) thorium. Dashed horizontal lines represent feed grades.

in systems comprised of multiple value minerals. In the case of the Nechalacho deposit it is important to differentiate the flotation of mixed particles containing fast-floating and slow-floating minerals (e.g. bastnäsite:allanite) from fully liberated particles when assessing flotation kinetics. The data obtained from QEMSCAN allows the

isolation of only “free” (>95% of particle surface comprised of a single mineral) particles for this purpose. After calculating recoveries of these “free” particles the data was fed to the same non-linear regression as discussed previously. The results of this analysis can be seen in Table 5. This data confirms the rapid flotation

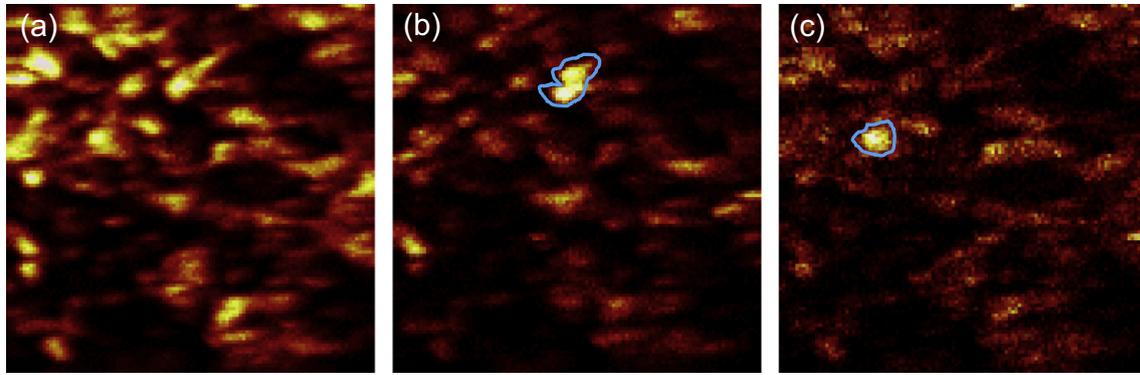


Fig. 9. Ion images from TOF-SIMS analysis representing 500 μm square sections for: (a) all ions collected, (b) Na, Al and K ions, and (c) all REE ions collected. Highlighted regions represent examples of the sub-regions selected for spectral comparison. Each image is 500 μm in width.

Table 6

Results of testing for statistically significant differences in surface loading of benzohydroxamic acid for various different populations of particles.

Benzohydroxamic acid		Higher relative intensity	
Population 1	Population 2	1	2
REM in Conc	REM in Tails	X	
Feldspar in Conc	Feldspar in Tails	X	
REM in Conc	Feldspar in Conc	X	
REM in Tails	Feldspar in Tails	–	–
REM + Feldspar in Conc (+Bz)	REM + Feldspar in Conc (+Pb +Bz)	–	–

Table 7

Results of testing for statistically significant differences in surface loading of Pb^{208}OH for various different populations of particles.

PbOH		Higher relative intensity	
Population 1	Population 2	1	2
REM in Conc	REM in Tails	X	
Feldspar in Conc	Feldspar in Tails	X	
REM in Conc	Feldspar in Conc	X	
REM in Tails	Feldspar in Tails	–	–

Table 8

Results of testing for statistically significant differences in surface loading of Pb^{208}O for various different populations of particles.

PbO		Higher relative intensity	
Population 1	Population 2	1	2
REM in Conc	REM in Tails	X	
Feldspar in Conc	Feldspar in Tails	X	
REM in Conc	Feldspar in Conc	X	
REM in Tails	Feldspar in Tails	X	

Table 9

Results of testing for statistically significant differences in surface loading of Pb^{208} for various different populations of particles.

Pb		Higher relative intensity	
Population 1	Population 2	1	2
REM in Conc	REM in Tails	X	
Feldspar in Conc	Feldspar in Tails	–	–
REM in Conc	Feldspar in Conc	–	–
REM in Tails	Feldspar in Tails	–	–

kinetics of both carbonates and niobates in this system and the general trend of decreasing flotation with decreasing solubility initially observed in Table 4.

3.6. Elemental grade and recovery

The grade and recovery of the different flotation conditions is shown in Fig. 8 on an elemental basis for Fe, Zr, light REE (La to Sm), heavy REE (Eu–Lu + Y) and U and Th. Fig. 8c indicates that the optimum condition for light REE concentration is the initial flotation stage, which agrees with the mineral results presented in previous sections. This initial flotation stage also results in the highest Fe grades (Fig. 8a). Fig. 8b and d show the highest recoveries for Zr and heavy REE occur after reconditioning with lead, corresponding to increased zircon recoveries. This is significant as the demand (and therefore price) is much higher for many heavy REE (Binnemans et al., 2013). Additionally, the response of the various REM in downstream processes is very different (e.g. leaching and digestion of zircon is much more difficult than similar processing of bastnäsite). These factors suggest that production of two flotation concentrates, one enriched in LREE-bearing minerals such as bastnäsite and the other enriched in HREE-bearing minerals such as zircon, may be advisable.

A final consideration for this flotation process is the concentration of deleterious elements along with the desired REM such as radioactive U and Th. Grades and recoveries of these two elements are shown in Fig. 8e and f. As the feed grades of U and Th in this work are 0.008% and 0.0032% respectively, it can be seen from these two figures that the flotation concentrates in all scenarios are enriched in both U and Th. This is unavoidable as U is found in fergusonite, columbite and zircon with Th occurring in fergusonite, columbite, monazite, zircon and allanite.

3.7. Effect of lead activator

The effect of the lead ion addition in this work was assessed using TOF-SIMS. Samples were taken from three products: the flotation pulp after reconditioning, the first concentrate produced after reconditioning, and the final tails. Each sample had four 500 μm \times 500 μm sections selected for spectral acquisition. The ion images produced were then filtered to select for the major gangue mineral feldspar (using Na, Al and K ion signals) as well as REM (using all identifiable REE ion signals). An example of a total ion image, Na–Al–K ion image and REE ion image may be seen in Fig. 9, along with an example of highlighted regions selected to analyse and compare ion spectra between grains. Sufficient grains from both feldspars and REM were selected in order to have statistically significant results. All results were tested for significance

using a T-test with a 95% confidence level. The relative intensity of signals for the benzohydroxamic acid collector, $Pb^{208}OH$, $Pb^{208}O$ and Pb^{208} were examined with the corresponding results summarized in Tables 6–9, respectively.

From this data it is possible to verify that the benzohydroxamic acid collector used in this work has specificity for REM over feldspars (Table 6). Similarly, the grains reporting to the concentrate have higher reagent surface loading than those in the tails, indicating that the amount of collector adsorbed to a particle is controlling whether it reports to the flotation concentrate. It can also be inferred that the lead ions are interacting with mineral surfaces via oxygen atoms [more significant signals for $PbOH$ and PbO species than for Pb (Tables 7–9)] which corresponds well with the traditional model of surface activation of silicates via Pb ions (Fuerstenau and Palmer, 1976). There is a clear discrimination between concentrate and tails for Pb indicating that particles reporting to the concentrate are doing so in response to Pb ions on their surface (Tables 7 and 8). The Pb ions also appear to preferentially adsorb onto the REM surfaces instead of feldspar (Tables 7 and 8). Finally, a comparison of the concentrates produced immediately after reconditioning with and without Pb ions shows no difference in collector loading (Table 6). This is significant as it suggests that there is excess collector present in the system after reconditioning so that the addition of Pb ions enables more particles to adsorb the benzohydroxamic acid collector instead of simply causing an increase in benzohydroxamic acid adsorption onto the particles which report to the concentrate. This is consistent with the observed large change in mass pull (Fig. 1) when Pb is added to the system.

3.8. Implications for industrial flotation

The grade, recovery and kinetic flotation results described in previous sections have implications for the design of a multiple stage industrial flotation process for this deposit. In envisioning such a process, an initial rougher flotation step with benzohydroxamic acid as the collector might be focused on light REM recovery with a secondary rougher using a secondary addition of collector to produce a concentrate more enriched in heavy REE. Scavenger flotation stages could potentially employ lead ions as an activator to maximize REM recovery (by targeting the recovery of less floatable REM). Depending on economic and environmental concerns (lead can be very environmentally concerning if present in the plant tailings stream), it might also be possible to use less collector, combined with lead ions, for the initial rougher flotation stages. Finally, as the work of Anderson (2015) suggests, lead is not the only metal cation which may be used as an activator for REM.

Based on the rapid kinetics of REM flotation with benzohydroxamic acid, the final grade and recovery of a combined concentrate (initial & post-reconditioning) was calculated including only the first 2 min of initial flotation and first 1 min of collection after reconditioning. The grade and recovery of these products are shown graphically in Fig. 10 and listed in Table 10. It can be seen

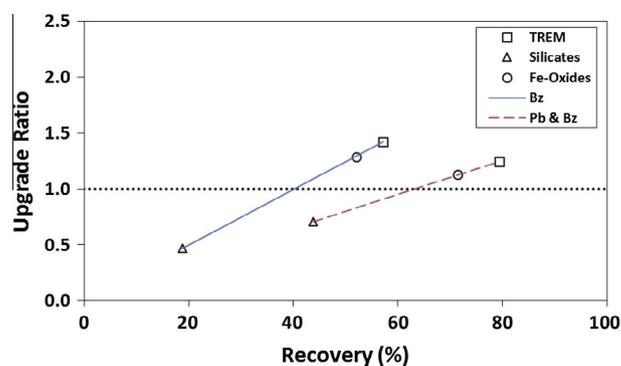


Fig. 10. Upgrade ratio versus recovery for combined products from initial flotation (first 2 min) combined with: post-reconditioning collection for 1 min with benzohydroxamic acid (Bz), and post-reconditioning collection for 1 min with lead ions and benzohydroxamic acid (Pb & Bz). The three minerals shown are total REM (square), quartz and feldspar (triangle), and iron oxides (circle).

that the reconditioning stage with only benzohydroxamic acid is the most selective (highest rejection of silicates), while reconditioning with the addition of lead ions achieves the highest recovery of REM. In both cases the grade of iron oxides is increased, indicating that the examined flotation reagent combinations are ineffective at rejecting this gangue mineral. A full metallurgical table of grades and recoveries for all three flotation conditions may be seen in Appendix A (Table A1).

The two optimal conditions (reconditioning with benzohydroxamic acid and reconditioning with both lead and benzohydroxamic acid) from Table 10 are shown in Fig. 11 for each individual REM. For each REM the idealized grade-recovery curve, as determined from QEMSCAN, is also shown. The idealized grade-recovery curve is produced by assuming the ideal situation where the mineral of interest is recovered sequentially as a function of particle surface exposure (degree to which the particle surface is composed of the mineral of interest) and then calculating the corresponding cumulative grade and recovery for each population of particles with decreasing surface exposure. Empirical flotation results rarely match up with this ideal grade-recovery curve but it is a useful comparative tool for the purposes of determining how to further improve the flotation process.

The implicit assumption in these calculations is that only the mineral of interest is recovered so the comparison of empirical results to the ideal curve in a system containing multiple value minerals will always have poorer grades than expected. Nevertheless, the results in Fig. 11b illustrate the effectiveness of the lead addition in pushing REM recoveries for every REM above 70%. Regrettably, this increased recovery is accompanied with significant decreases in grade relative to the conditions shown in Fig. 11a. Fig. 11 illustrates the differences between these two reagent conditions and provides useful insight into the possibility of developing distinct separation processes for the different REM in this deposit based on varying flotation responses.

Table 10

Grade and recovery of combined flotation concentrates.

Number	Product	Reagent	Total REM		Silicates		Fe-oxides	
			Recovery	Grade	Recovery	Grade	Recovery	Grade
1	First Stage (2 min)	Bz	32.7	59.8	12.3	21.1	32.5	14.0
2	Post-Recondition (1 min)	Bz	24.5	66.5	6.5	16.4	19.5	12.3
3	Post-Recondition (1 min)	Pb & Bz	46.7	51.4	31.4	33.4	39.0	10.0
	Combined 1 (1 & 2)	Bz	57.2	62.5	18.8	19.2	52.0	13.3
	Combined 2 (1 & 3)	Pb & Bz	79.5	54.6	43.7	28.7	71.5	11.5
	Feed			43.8		40.8		10.2

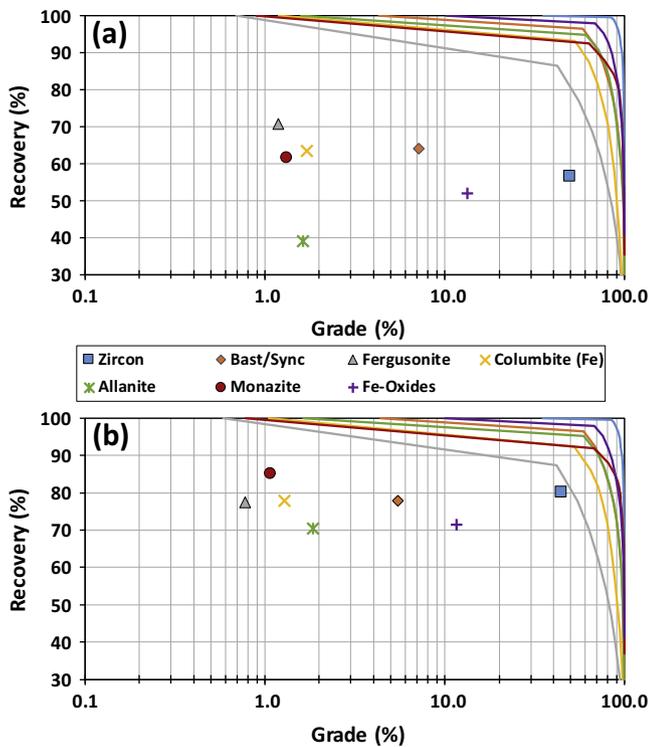


Fig. 11. Optimum grade–recovery results of REM compared to ideal grade–recovery as determined by QEMSCAN. Results shown are for: (a) first stage flotation with benzohydroxamic acid for 2 min followed by reconditioning with additional benzohydroxamic acid and floating for 1 min (+ Bz), and (b) first stage flotation with benzohydroxamic acid for 2 min followed by reconditioning with lead ions and additional benzohydroxamic acid and floating for 1 min (+Pb +Bz).

4. Conclusions

This work presents the results of flotation experiments conducted on a pre-concentrated REM feed to evaluate different reagent combinations including initial flotation using a benzohydroxamic acid collector, reconditioning with additional collector and reconditioning with an addition of lead as an activator followed by benzohydroxamic acid. It is important to note that the goal of this work is to determine fundamental flotation properties of the different REM in the Nechalacho deposit. As such, the process investigated here is not indicative in any way of the current process design for this deposit. The conclusions of this work are as follows:

- The relative flotation kinetics of the REM in this deposit with benzohydroxamic acid (in decreasing order) are:
 - bastnäsite > fergusonite > synchysite > columbite(Fe) > monazite > zircon > allanite.

- Benzohydroxamic acid is a much more effective collector for REM with relatively high degrees of solubility and relatively high REE contents (i.e. bastnäsite vs. allanite).
- A secondary addition of benzohydroxamic acid results in improved flotation of important REM such as zircon.
- The addition of lead ions as an activator increases the recovery of less floatable REM such as zircon and allanite while also increasing the recovery of silicate gangue minerals (with some selectivity for quartz over feldspar).
- TOF-SIMS results indicate that the lead addition increases the number of particles able to adsorb benzohydroxamic acid, thereby resulting in a significantly increased mass pull.
- The results of this work support the design of a flotation process for this deposit which does not treat all REM as having identical flotation behaviours. A staged addition of benzohydroxamic acid coupled with the addition of activating ions may be the most efficient flotation process for this deposit.

5. Future work

In order to continue to expand the knowledge base surrounding the REM in this deposit the following future work should be carried out:

- Locked cycle flotation tests to determine the required collector dosages for a multiple stage flotation process as well as the persistence of both benzohydroxamic acid and lead on the surfaces of both REM and gangue minerals.
- Investigate proper depressants to selectively depress silicate gangue and iron oxides in the presence of both benzohydroxamic acid and lead ions.
- Investigate alternate activators for silicate REM with less potential impact on the environment.

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Appendix A

See Table A1.

Table A1
Cumulative grade and recoveries for all three flotation conditions.

Condition	Time (min)	REM		Silicates		Fe-Oxides	
		Cum. Grade (%)	Cum. Recovery (%)	Cum. Grade (%)	Cum. Recovery (%)	Cum. Grade (%)	Cum. Recovery (%)
No Bz	0.5	60.2	15.7	20.1	5.8	14.3	16.1
	1	59.6	22.8	20.8	8.8	14.3	23.8
	2	58.9	29.7	21.5	12.0	14.4	31.4
	5	57.6	33.4	23.2	14.9	14.2	35.9
	5.5	56.5	34.1	24.3	16.2	14.1	36.8
	6	55.8	34.5	25.1	17.1	14.0	37.4

Table A1 (continued)

Condition	Time (min)	REM		Silicates		Fe-Oxides	
		Cum. Grade (%)	Cum. Recovery (%)	Cum. Grade (%)	Cum. Recovery (%)	Cum. Grade (%)	Cum. Recovery (%)
+Bz	12	54.9	34.9	26.0	18.2	13.8	38.1
	Tails	40.2	65.1	45.6	81.8	8.8	61.9
	0.5	60.5	14.8	19.1	5.1	14.6	15.4
	1	59.8	21.4	20.1	7.8	14.5	22.1
	2	59.1	28.1	21.3	11.0	14.3	29.0
	5	57.8	31.6	22.9	13.6	14.2	33.1
	5.5	60.7	47.3	20.5	17.4	13.6	45.3
	6	61.3	56.1	20.3	20.1	13.4	52.6
	12	61.1	64.3	20.9	23.9	13.0	58.7
	Tails	29.1	35.7	57.3	76.1	7.8	41.3
+Pb +Bz	0.5	64.1	21.0	17.5	6.0	13.3	18.8
	1	62.1	31.4	19.1	9.9	13.7	28.5
	2	61.1	40.5	20.5	13.9	13.5	37.1
	5	59.8	43.8	21.9	16.4	13.4	40.8
	5.5	58.2	78.7	25.0	34.9	11.8	67.4
	6	55.2	90.5	28.3	47.9	11.5	79.8
	12	50.8	96.5	33.0	64.7	11.1	89.0
	Tails	8.4	3.5	80.6	35.3	6.1	11.0

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