Research Article

Synthesis and characterization of hydroxamic acid N,3-dihydroxy-2-naphthamide and its copper (II) complex per keto/enol forms and rare earth flotation

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Abstract

Flotation is the most common beneficiation process used for separating minerals, but for rare earth minerals (REMs), performance can suffer due to the dilute nature of the rare earth elements. Furthermore, the REMs tend to possess smaller grain sizes, making the use of traditional flotation cells difficult if total liberation is needed. Consequently, improved efficiencies are needed for extracting REMs from various sources. For these systems, hydroxamic acids are commonly used as flotation collectors. Two such hydroxamic collectors were studied in this work: salicylhydroxamic acid (SHA) and N,3-dihydroxy-2-naphthamide (H2O5). Because there is no documented synthesis route for H2O5, several synthesis approaches were examined. Furthermore, because there is no information on H2O5, important structural and characteristic data was gathered regarding its (1) preferred structural isomer as a Cu^{2+} complex and (2) electrostatic potential values of the possible dentate groups in different tautomeric forms, thereby allowing H2O5 to be compared to SHA, particularly regarding flotation behavior. Hydrogen nuclear magnetic resonance (H-NMR), Laser Raman Spectroscopy (LRS), and predominantly Fourier-Transform Infrared (FT-IR) spectroscopy showed that both SHA and H2O5 preferred to be keto tautomers when uncomplexed; however, once chelated to Cu^{2+} ions, the collectors adopted enol forms. Molecular modeling using Spartan software showed an increase in the electrostatic potential of the possible dentate groups in both molecules for the enol form. H2O5 also resulted in an increased recovery by flotation of REMs of about 23% compared to SHA at similar reagent dosages.

Keywords: Rare earth minerals, flotation, H2O5, SHA, isomers, tautomers

INTRODUCTION

Rare earth minerals

The lanthanides are a series of elements ranging from lanthanum to lutetium, with atomic numbers 57 to 71 in the periodic table. Together with scandium and yttrium (atomic numbers 21 and 39, respectively), they are collectively referred to as Rare earth elements (REEs). Rare earth minerals (REMs) are so named because they are usually comprised of one or two REEs in majority amounts, predominantly as either oxides, carbonates, phosphates, or silicates, respectively referred to as REOs, RECs, REPs, and RESs. For example, xenotime (YPO_4) is yttrium-bearing REP, and bastnaesite [$(Ce,La)CO_3X$] is a REC containing cerium and lanthanum, where X is usually fluoride (F) but can be hydroxide (OH). However, REMs are often solid solutions of other REEs, usually in smaller amounts and typically as either light REEs (LREEs, atomic numbers 57 to 63) or heavy REEs (HREEs, atomic numbers 64 to 71). In this regard, xenotime is often a source of other HREEs, particularly gadolinium, terbium, dysprosium, erbium, and ytterbium; likewise, bastnaesite is known to contain other LREEs, particularly neodymium, praseodymium, and samarium[1].

REEs are chemically and physically similar due predominantly to subtle differences in their f-shell orbitals[2]. Perhaps the most important physical property is referred to as lanthanide contraction (LC), such that the REEs decrease in size with increasing atomic number; however, size is also dependent on the REE coordination number (CN) defined by the mineral type (e.g., REO, REC, REP, and RES) which, of course, is a chemical property. Consequently, REMs often possess chemical and physical properties that are similar, particularly if the REMs are the same type and the REEs they contain are similar. This usually makes both REM separations from ores straightforward and cost-effective; however, the individual separations of the REEs are usually inefficient and fraught with significant challenges. Current best practices, therefore, generally employ successive metallurgical processing with bulk REM concentration steps, such as froth flotation, followed by individual REE separation steps, such as leaching and resin adsorption, prior to producing the individual REEs pyrometallurgically[3].

Flotation

Flotation, which is short for froth flotation, is a beneficiation process that separates mineral particles in a pulp based on differences in hydrophobicity. For it to work, gas bubbles are injected into the slurry and attach to hydrophobic particles, causing them to float into a froth at the pulp interface, which is then removed as a concentrate. Hydrophilic particles remain in the pulp as gangue minerals and are removed as tailings. Interestingly, this physical separation is chemically enhanced to control various properties such as surface tension and surface charge. For example, frothers are chemicals used to control the surface tension of water and thereby stabilize the froth, whereas collectors are used to impart hydrophobicity to selected minerals and make them amenable to flotation. Likewise, depressants and activators are chemicals used to modify mineral surfaces to either prevent or enable collector adsorption, typically by changing their surface charge. Furthermore, REM flotation can be difficult to do in the industry due to several factors, including ores having complex mineralogy and/or containing a variety of REMs. In addition, REMs may have surface chemistries such as gangue minerals and/or possess liberation sizes that are too fine for flotation to be effective. Many of these difficulties can be overcome using novel collectors designed for this purpose by attempting to selectively maximize changes in the surface properties of the target particles[4].

For REM flotation, it is well established that hydroxamic acids (HAs) are more selective than fatty acid (FA) collectors[5,6]. Consequently, HAs are more commonly used for REMs[7], and their use is attributed to their ability to chelate with REEs. Two common FA and HA collectors are oleic FA (OFA) and octyl HA (OHA), respectively. The interactions of these collectors with REM surfaces have been studied in detail using various spectroscopic techniques such as X-ray photoelectron spectroscopy (XPS), Fourier-transform

infrared spectroscopy (FT-IR), laser Raman spectroscopy (LRS), and scanning electron microscope (SEM) analysis to determine adsorption mechanisms from the plethora of resulting information[8,9].

In efforts to improve flotation performance, unique HAs have been studied for comparison to OHA. For example, researchers examined naphthalenic HA (NHA) for bastnaesite flotation and found it did not offer significant advantages. They concluded that even more selective collectors were needed[10]. Hence, collectors, such as salicylhydroxamic acid (SHA), have recently been examined[11-14]. It was collectively concluded from these studies that LC and CN played critical roles[2,4]. In general, RECs have CN = 10 and, therefore, possess the largest cationic diameters. By comparison, REOs have CN = 7 or 6 and thus have the smallest cationic diameters, whereas REPs have CN = 9 or 8 and thus have cationic diameters between. Interestingly, SHA adsorbed the strongest on the REMs with diameters approximately equal to its hydroxamate chelating size. Current studies are being conducted on RESs to see how LC and CN influence their flotation behavior[15] and determine if collector blends can be accordingly developed to maximize flotation performance no matter what REM types are in the ore[4,16]. In regards to these publications and ongoing efforts, particularly the challenge that more selective collectors are needed, this study with N,3-dihydroxy-2-naphthamide (H2O5) was undertaken.

HA collectors

H2O5 was first synthesized by the Baotou Research Institute of Rare Earths in China[17]. While SHA (N,2-dihydroxybenzamide) is an analog of H2O5 and is rather common due to its promise in medicine as an antimalarial drug, H2O5 is hard to come by. Currently, there is no information on its laboratory preparation. This paper offers a route to synthesize H2O5 from readily available precursors.

The synthesis of H2O5 is relatively straightforward since HAs can be formed from esters under alkaline conditions[18]. The procedure for synthesizing H2O5 is partially derived from a qualitative test used to detect the presence of esters in a solution. The test involves treating an ester-containing solution with an excess of hydroxylamine in the presence of a strong base. This converts the ester into a HA. In the test, the newly formed HA is treated with a ferric chloride solution. HAs react with Fe^{3+} salts to form vibrantly colored solutions, thus indicating the initial presence of esters. To increase the yield of the ester conversion to an HA, the synthesis described in this article deviated from the procedures of the traditional qualitative test by using a microwave reactor in alkaline conditions[19]. Because H2O5 does not contain any base-sensitive functional groups, this synthetic method described below is preferable to other more complex methods that perform the conversion via an anhydride or other routes.

One analog to H2O5 that is currently being studied as a collector is SHA, which has been noted for its effectiveness in REM flotation[20,21]. The only difference between the two collectors is the organic backbone. SHA contains a benzyl group, whereas H2O5 contains a naphthyl group in a study on bastnaesite ores in which the effect on zeta potential and micro-flotation was examined[10]. As occurs with HAs in general, both SHA and H2O5 contain four primary active electronegative groups, which can potentially participate in coordination chemistry. Through a tautomerization mechanism, it is extremely likely that they resonate between the amide and imidic forms[22]. For the imidic form, the Pauling standardization of electronegativity was used to show that the most electronegative atom in the HA structure is the nitrogen with a value of 4.03, whereas the oxygen in the N-OH group calculated to be 3.69, the imidic OH group was determined at 3.85, and the phenolic OH group was found to be 3.80. It was concluded that H2O5 coordinated via the imidic and hydroxamic oxygen atoms[10]. By comparison, Electron Spin Resonance (ESR) spectroscopy has been used, and it was found that Cu^{2+} complexes of HAs form complexes with the carbonyl and hydroxamine oxygens[23]. However, it is noted that their study focused on C-methyl-N-phenyl HA, which is a secondary

hydroxamate. Secondary HAs, while not possessing the same metal ion binding capability as primary HAs, can still form complexes[24]. Consequently, this characterization procedure is used to examine H2O5 and SHA Cu^{2+} complexes and whether they coordinate via the route calculated by[10] in order to shed some light on their selectivity.

HAs could rotate across the single C–N bond to form Keto E and Z stereoisomers [Figure 1, top]. It was discovered that with protic solvents such as water, the Keto Z conformation was the most prevalent due to the stabilization of the intermolecular carbonyl and hydroxyl bond[25]. In addition, HAs could tautomerize[26] and thereby form tautomers, with the uncharged version being the major species present [Figure 1, bottom]. The two tautomers are also isomers; however, in this case, a double C=N bond prevails, restraining rotation and resulting in the Enol form. While HAs could be considered amides and thus would tautomerize from the amide to the imidic form, most researchers on the subject use the keto-enol nomenclature. Thus, from this point forward, the latter convention will be used.

Based on calculated electronegativities of the nitrogen and oxygens in a hydroxamic complex, to achieve coordination, the hydroxamic group must tautomerize to its enol form[10]. The process of determining which form an amide or HA takes is complex because small external effects can drastically change the absolute positions of characteristic bonds[27]. In this regard, external effects include but are not limited to the electronic environment, ionic strength, and hydrogen bonding; hence, the bonds that are used to characterize these compounds must be chosen with care. However, by focusing on the carbonyl bond and the C=N bond, the most prevalent tautomer can be determined[28,29]. Furthermore, this information might help discern the mechanism for HA adsorption at REM surfaces.

EXPERIMENTAL DETAILS
H2O5 collector synthesis
The procedure for creating H2O5 is as follows. First, 2.5 mmols of 3-Hydroxy-2-naphthoic acid (BON acid) was sourced from Alfa Aesar and added to roughly 10 mL of methanol (MeOH). A catalytic amount of p-toluenesulfonic acid was then added. Subsequently, 3-Å molecular sieves, which were previously dried in an oven overnight at 120 ℃, were added to the boiling flask to help absorb water, which is a byproduct of the esterification process. Water can lead to unwanted hydrolysis of the product. The mixture was refluxed for 8-12 h. After refluxing, the flask was vacuum filtered to remove the sieves. The solution was allowed to cool in the freezer for 1-4 h. The first crystals of the methyl ester were filtered off. Next, the solution was placed under an air stream to evaporate off the MeOH to recover the rest of the ester product.

The solids were then dissolved in dichloromethane (DCM) and washed with copious amounts of saturated sodium bicarbonate solution to remove as much of the remaining BON acid as possible. The DCM solution was then evaporated. The product was approximately 2 mmols of methyl 3-hydroxy-2-naphthoate, which represents an 80% yield. The product took the form of thin needle-like crystals and had a slight minty smell similar to oil of wintergreen. The melting point of the compound was 71.8-72.3 ℃, which corresponded to the literature value of 73-75 ℃. Next, 2.5 mmols of the resulting methyl 3-hydroxy-2-naphthoate was dissolved in 20 mL of MeOH.

In a separate beaker, 15 mmols of hydroxylammonium hydrochloride was dissolved in MeOH. To this solution, a stoichiometric excess of potassium hydroxide (KOH) was added. A white precipitate of potassium chloride (KCl) immediately formed and was vacuum filtered, thereby yielding a hydroxylamine solution. This was mixed in a microwave reactor with the MeOH/methyl 3-hydroxy-2-naphthoate solution with 30 mmols of additional KOH. With a microwave set at 2,450 MHz and 150 W power, a reaction was
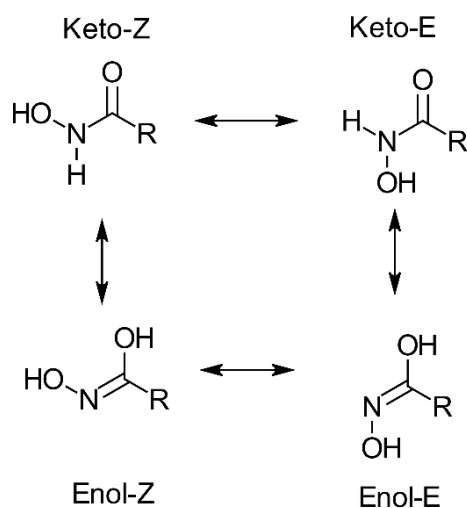
Figure 1. Conformational and tautomeric isomers of hydroxamic acid.

conducted for six minutes and cooled for five minutes. Excess KOH was then neutralized to pH 7 using a dilute hydrochloric acid to prevent decomposition of the newly formed product. Next, the precipitate was vacuum filtered, washed with cold water and cold DCM, and run through a silica chromatography column so that the HA fraction could be collected. After the eluent was evaporated, the dry product was recrystallized using ethanol and then further dried under vacuum to remove residual ethanol.

About 1 mmol of the product was recovered after recrystallization, which represents ~40% molar yield based on the starting material. The resulting H_2O_5 was verified using Hydrogen nuclear magnetic resonance (H-NMR), LRS, and FT-IR spectroscopy. H-NMR was conducted with a Bruker 300 MHz DPX Advance I NMR Spectrometer, and LRS spectra were obtained with a Renishaw InVia MicroRaman system using a HeNe laser. FT-IR spectra were obtained using a Nicolet iS5 ATR FT-IR spectrometer.

H-NMR results were determined using 6-31G* calculations because we believed they would correlate better with the Spartan calculations which are presented and discussed later. H-NMR indicated the melting point of the product was 166.8-170.1 °C with the following information: 1H NMR [300 MHZ, dimethyl sulfoxide (DMSO)-d6 w/0.03% v/v tetramethylsilane (TMS)] δ 11.52 (2H, s), 9.41 (1H, s), 8.32 (1H, s), 7.85-7.83 (1H, d), 7.75-7.72 (1H, d), 7.51-7.46 (1H, m), 7.36-7.33 (1H, m), 7.31-7.28 (1H, m), where DMSO is dimethyl sulfoxide and TMS is tetramethyl silane which are used to investigate the quality of the synthesized H_2O_5. LRS spectra were also found to be complementary to FT-IR spectra due to their respective symmetry-asymmetry relationship. While these results suggest the product is good quality, subsequent discussions emphasize only the FT-IR and Spartan results.

Metal complex synthesis

SHA and copper sulfate, both of 99% purity, were obtained from Alfa Aesar. A saturated solution of copper sulfate in 1:4 MeOH and water solvent was prepared and placed in a burette for titration. Using separate beakers, both the SHA and synthesized H_2O_5 were dissolved in MeOH. While stirring, the copper sulfate solution was added dropwise to each of the SHA and H_2O_5 solutions. It is important to note that the MeOH in the copper sulfate solution prevented SHA and H_2O_5 precipitates from crashing out in overly aqueous conditions. The solutions were stirred for 30 min and then vacuum filtered. After washing the products with water and MeOH, they were dried in an oven at 90 °C, resulting in fine, deep-green powders

that were soluble in DMSO.

Flotation

For this study, an REE-bearing ore was obtained from Rare Element Resources' Bear Lodge Project in northeast Wyoming. The ore was chosen because it contained only trace amounts of uranium and thorium (< 0.05%). Upon receiving the ore sample, it was homogenized and split into approximately 1.2 kg samples for use in flotation experiments. Any remaining sample was saved for analysis.

Previous experimental work on SHA, both published and unpublished, has been performed at Montana Tech. These experiments will be used as a comparison for flotation performance of SHA *vs.* H_2O_5. Experiments were performed using simple kinetics test (SKT) experimental procedures[30] and a 2-factorial experimental design varying three factors and midpoint experiments with three replicates for a total of 11 experiments. In the unpublished work, a 2-factorial three-factor experimental design, which varied superficial gas velocity, pH, and collector dosage, was created. The published work tested a SHA collector dosage of 333 g/tonne at a pH of 7.5 and varied milling time, impeller rotor speed, and superficial gas velocity. The collector dosage was not optimized, but unpublished work had established that a slurry pH of 7.5 resulted in the optimized recovery of REMs. The unpublished and published experimental designs and operating parameters that were constant are shown in Table 1. Seven flotation experiments for H_2O_5 were performed as a 2-factorial experimental design that varied two factors, pH and collector dosage, and three midpoint replicate experiments. The H_2O_5 experimental design is shown in Table 2.

Slurries were prepared by grinding the samples in a rod mill at 60% solids by weight using deionized water. The ore was ground for 19 min for the unpublished SHA experiments and the H_2O_5 experiments and between 10 and 19 min for the published SHA experiments. Slurries were then added to a 6-liter, cylindrical sub-aerated flotation cell from FLSmidth and diluted with more deionized water to 17%-18% solids by weight. At this time, a 0.4 L feed sample of the slurry was taken, wet-sieved, and saved for analysis. Afterward, the pH was adjusted with drops of NaOH (1 M) or HCl (1 M) as needed.

Methyl isobutyl carbinol (MIBC) was used as a frother and was initially added to the cell at 125 g/tonne. Collector dosages, as shown in Tables 1 and 2, were then added directly to the pulp zone of the flotation cell. Additionally, several SHA experiments were run at a pH of 7.5 and higher collector dosages of 416.7 g/tonne matching the high value from the unpublished work and 750 g/tonne which corresponded to the high value from the H_2O_5 experimental design for comparison. After 15 min of conditioning, flotation was performed based on the SKT designed by AminPro[30]. With SKT procedures, flotation is conducted for thirty minutes with concentrate samples being collected for 45 s (Con 1), 2 min (Con 2), 8 min (Con 3), and 30 min (Con 4) to allow for the separation of fast floating and slow floating minerals. Flotation cell operating parameters are shown in Tables 1 and 2. The slurry level in the flotation cell was controlled by a float valve connected to a 20-L conditioning tank containing a make-up solution of MIBC at the desired pH.

All samples were characterized with a SEM using Mineral Liberation Analysis (MLA) software. The SEM was a LEO 14.30VP with an electron beam produced at 25 kV and an Ametek Apollo 40 Energy Dispersive X-ray (EDX) detector. Samples were prepared using a cross-mount procedure in which they were mixed with carbon and then epoxy, resulting in a sample block. The block was then cut in half and remounted with additional epoxy such that the cross-sectioned face would be exposed and analyzed. This procedure avoids particulate orientation issues such that light and heavy, in addition to small and large particles, would be random. After the resulting pucks were coarsely polished using 400-μm to 180-μm grit paper and fine polished with powder ranging from 15-μm alumina to 0.3-μm diamond paste, they were carbon coated,

Table 1. SHA flotation experiments

SHA	Experiment	pH	Dosage (g/tonne)	Jg (cm³/s)	Grind time (min)	Rotor speed (rpm)
Unpublished	1	9.0	83.3	0.51	19	2,000
	2	9.0	416.7	0.51	19	2,000
	3	9.0	83.3	1.03	19	2,000
	4	9.0	416.7	1.03	19	2,000
	5	7.5	250	0.77	19	2,000
	6	7.5	250	0.77	19	2,000
	7	7.5	250	0.77	19	2,000
	8	6.0	83.3	0.51	19	2,000
	9	6.0	416.7	0.51	19	2,000
	10	6.0	83.3	1.03	19	2,000
	11	6.0	416.7	1.03	19	2,000
Published	1	7.5	333.3	0.41	10	1,800
	2	7.5	333.3	0.41	10	2,200
	3	7.5	333.3	0.41	19	2,200
	4	7.5	333.3	0.77	10	1,800
	5	7.5	333.3	0.77	10	2,200
	6	7.5	333.3	0.77	19	1,800
	7	7.5	333.3	0.77	19	2,200
	8	7.5	333.3	0.59	14.5	2,000
	9	7.5	333.3	0.59	14.5	2,000
	10	7.5	333.3	0.59	14.5	2,000
	11	7.5	333.3	0.41	10	1,800

The experiments were designed based on a 2-factorial methodology and varied three factors with three midpoint experiments. SHA: Salicylhydroxamic acid.

Table 2. H2O5 flotation experiments

H2O5	Experiment	pH	Dosage (g/tonne)	Jg (cm³/s)	Grind time (min)	Rotor speed (rpm)
	1	11.0	750	1.03	19	2,200
	2	6.0	750	1.03	19	2,200
	3	11.0	250	1.03	19	2,200
	4	6.0	250	1.03	19	2,200
	5	8.5	500	1.03	19	2,200
	6	8.5	500	1.03	19	2,200
	7	8.5	500	1.03	19	2,200

The experiments were designed based on a 2-factorial methodology and varied two factors with three midpoint experiments. H2O5: N,3-dihydroxy-2-naphthamide.

placed in the sample chamber and analyzed as soon as the chamber reached an appropriate vacuum. Results indicated that the original sample contained ~2% REE or ~3% REM, with the three major minerals being REO [cerianite, CeO_2], REC [parasite, $Ca(Ce,La,Nd)_2(CO_3)_3F_2$], and REP [monazite, $(Ce,La)PO_4$]. Furthermore, the REMs consisted of approximately 90% LREEs and 10% HREEs. Results for the sized feed, timed concentrate, and tail samples were used to determine the mineralogy, liberation, association, grade, and recovery for each flotation experiment.

RESULTS AND DISCUSSIONS

H2O5 collector synthesis

While the above method was successful in synthesizing H2O5 from BON acid, the product does contain an unknown minor impurity. This side-product fluoresces heavily using the Renishaw inVia confocal Laser Raman microscope with an excitation frequency of 532 nm. It is speculated that it might be due to chromophore substitutions to the compound. It was found that these substitutions became more prominent after running the product through the silica column; however, the impurity does not necessarily arise from this step. Finally, because a near stoichiometric amount of complex forms after chelation with the copper salt, the impurity does not seem to have a large effect on the ability of the hydroxamic group to bind to the Cu^{2+} ions.

H2O5 and SHA comparisons

Because H2O5 and SHA have the same functional groups [Figure 2A and B, top], it would be expected that they would have similar infrared (IR) spectra [Figure 2A and B, bottom]. Both H2O5 and SHA have strong carbonyl peaks with the characteristic secondary amide double peak around 1,530 cm⁻¹. Looking at the higher wavenumbers, both compounds contain a broad peak around the 3,100 cm⁻¹ region that likely contains degenerate peaks of the nitrogen and the alcohol bonds. However, two peaks at 2,687 and 2,556 cm⁻¹ appear prominently with SHA but are only visible as shoulders with H2O5. This difference could be caused by intramolecular hydrogen bonding, which broadens the bands due to the multitude of bond strengths from the autoprotolysis reactions.

Collector group elements

FT-IR spectra were also collected for the copper complexes as solids and compared to their protonated forms. Spectral comparisons of the H2O5-Cu^{2+} complex and SHA-Cu^{2+} complex are shown in Figures 3 and 4, respectively. Table 3 highlights some of the characteristic differences between the two collectors and their organometallic complexes. Specifically, five bonds are examined because they strongly indicate if tautomerization occurs upon complexation: the C–H stretch, 2° Amide C–N, N–H stretch, C=O vibration, and C=N stretch[31]. The results indicate that the C–H stretch changes very little after complexing with Cu^{2+}. For example, with H2O5, it decreases from 3,055 to 3,050 cm⁻¹, but in the SHA sample, there was an increase from 3,049 to 3,064 cm⁻¹. Likewise, after complexing with Cu^{2+}, the Amide C–N vibration changes very little in SHA (increasing from 1,521 to 1,525 cm⁻¹); however, in H2O5, the change is significant (decreasing from 1,534 to 1,497 cm⁻¹). Most importantly, though, the N–H stretch and C=O vibrations near 3,280 cm⁻¹ and 1,615 cm⁻¹, respectively, disappear when both collectors are copper-complexed. Furthermore, for both collectors, the C=N stretch near 1,580 cm⁻¹ appears when they are complexed.

All four of the compounds exhibit the characteristic secondary amine double peak contour near 1,515 cm⁻¹. From the contour of the secondary amine peaks, it can be deduced that these compounds likely take the Keto-Z form, as earlier shown in Figure 1[27]. Because the C=N stretch is very prevalent and the C=O stretch is very repressed in both Cu-complexes, it is likely that the enol tautomer takes precedence in the complex[28,29]. It is, therefore, concluded that H2O5 forms the two tautomers shown in Figure 5, with the Keto-Z form on the left and the Enol-Z form on the right[Figure 1, left]. The likely dentate groups are designated in red. The same would be concluded for SHA.

The likely groups are inferred based on the Pauling electronegativity standardization performed by[10] and through modeling via Spartan, a molecular modeling program. It is noted that, in both of these forms, the two oxygen atoms nearest the amine group are the most likely to complex with metal ions. This is not surprising because HAs are particularly known for their chelation reactions. Thus, with respect to REEs, H2O5 and SHA are likely to bond with REM surfaces by reacting through these oxygens, leading to either a

Table 3. Characteristic FT-IR peaks of HA collectors and their complexes

| Compound	C–H	2° Amide C–N	N–H stretch	C=O	C=N stretch
H2O5	3,055	1,534	3,272	1,631	-
SHA	3,049	1,521	3,285	1,600	-
Cu²⁺·H2O5	3,050	1,497	-	-	1,591
Cu²⁺·SHA	3,064	1,525	-	-	1,567

FT-IR: Fourier-transform infrared; HA: hydroxamic acid; H2O5: N,3-dihydroxy-2-naphthamide; SHA: salicylhydroxamic acid.
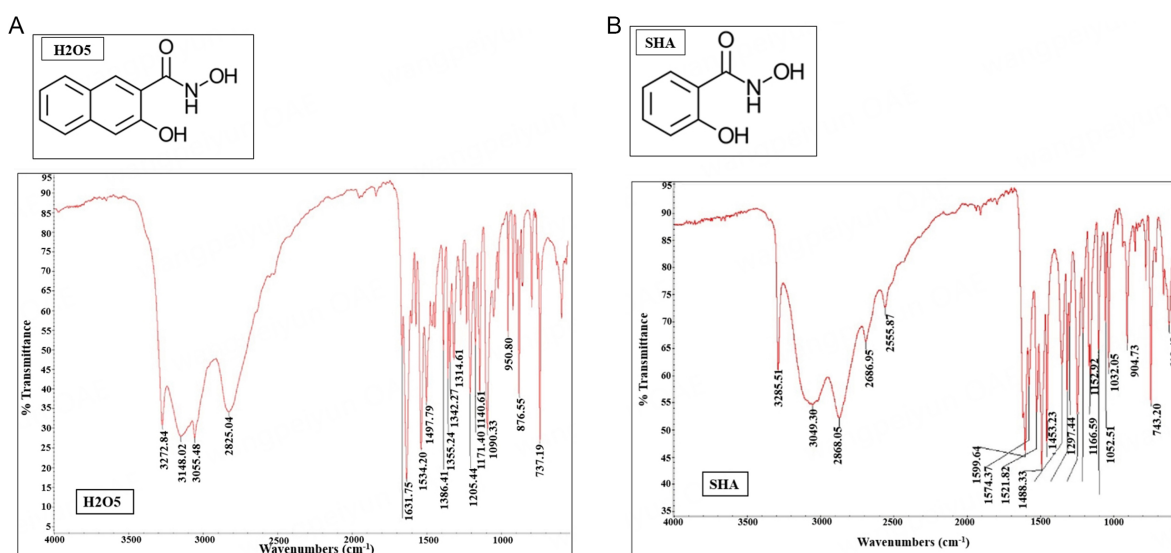

Figure 2. (A) Structure and FT-IR spectra of synthesized H2O5; (B) Structure and FT-IR spectra of synthesized SHA. FT-IR: Fourier-transform infrared; H2O5: N,3-dihydroxy-2-naphthamide; SHA: salicylhydroxamic acid.
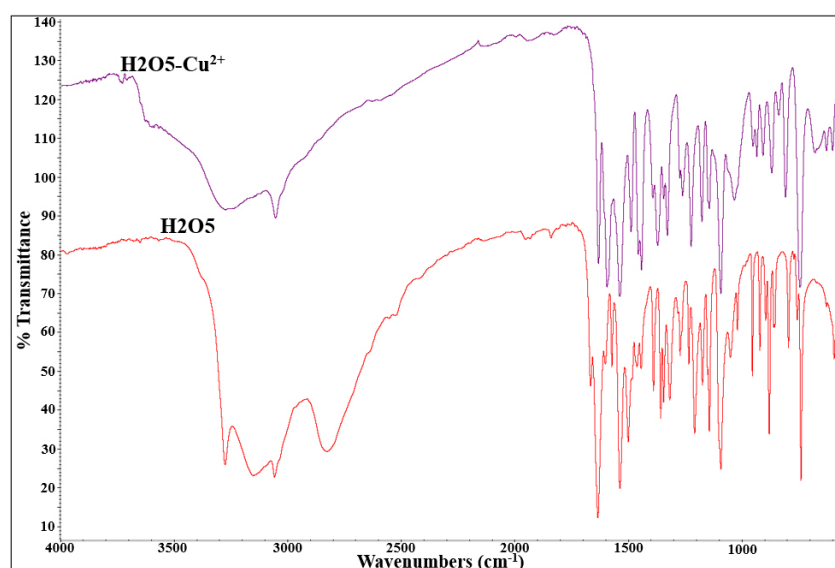
Figure 3. A comparison of H2O5-Cu²⁺ complex (top) with H2O5 (bottom). H2O5: N,3-dihydroxy-2-naphthamide.
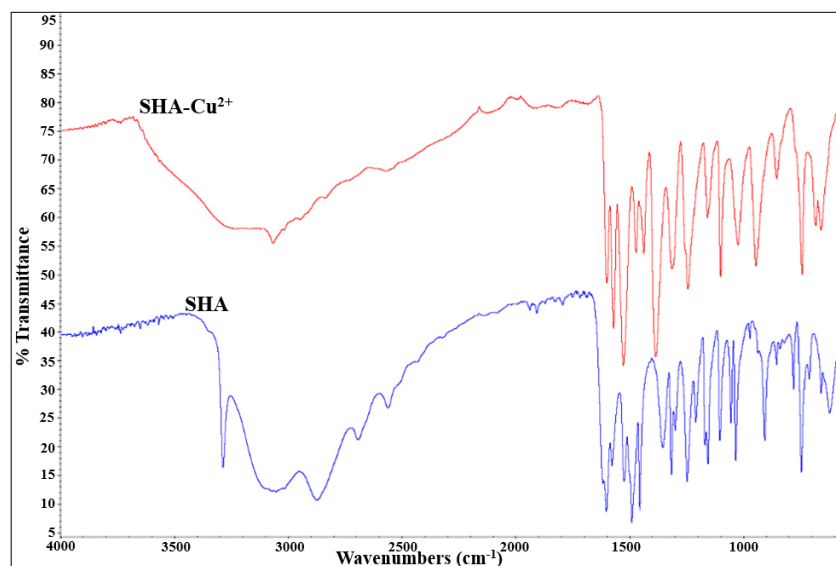
Figure 4. A comparison of SHA-Cu^{2+} complex (top) with SHA (bottom). SHA: Salicylhydroxamic acid.
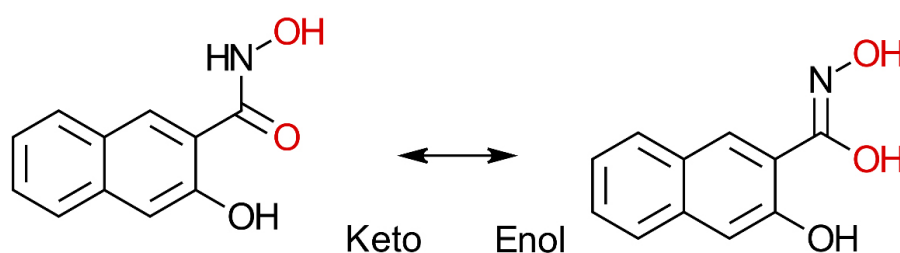
Figure 5. The tautomerization of H2O5 with the most electronegative atoms in red. H2O5: N,3-dihydroxy-2-naphthamide.

chemisorbed or surface precipitated collector or a combination of the two. A mechanism has been presented along these lines[2,4,11-14] and is the subject of continuing investigations[15,16].

In this regard, Spartan software was used to model H2O5 and SHA using Hartree-Fock 6-31G* basis set in a simulated aqueous environment to prevent false charge build-up that can accompany calculations in a vacuum environment. Interestingly, resulting models indicate that the two oxygen atoms on H2O5 are slightly more electronegative than those on SHA, suggesting H2O5 might be a better collector than SHA albeit it could also suggest that it becomes less selective too. The electrostatic potential data for the tautomers of H2O5 and SHA are given in Table 4 for the individual atoms of the functional group: hydroxamic oxygen, nitrogen, carbonyl oxygen, and phenolic oxygen, with various levels of deprotonation. The most notable data point is the large jump in the potential of the carbonyl oxygen in the Enol trianion form. Consequently, it is believed that this tautomer is the form that coordinates the strongest with REEs; hence, the isosurfaces for H2O5 and SHA for Enol anion tautomers are shown in Figures 6 and 7. These maps show the surface potential around an isovalue of 0.002 with units, being KJ/mol and spherical markers showing inaccessibility along the surface.

Flotation comparison

Sample particle size distributions for the three milling times, as determined from MLA [Figure 8].

Table 4. Spartan molecular modeling of electrostatic potentials of H2O5 and SHA group elements in various levels of deprotonation and tautomer forms

|	Keto Z anion	Enol E anion	Keto Z dianion	Enol E-3
H2O5				
O1 -hydroxamic	-0.804	-0.671	-0.837	-0.856
N	-0.244	-0.432	-0.206	-0.717
O2 - carbonyl	-0.76	-0.773	-0.786	-1.041
O3- phenolic	-0.723	-0.705	-0.863	0.827
SHA				
O1 -hydroxamic	-0.808	-0.507	-0.753	-0.797
N	-0.237	-0.397	-0.055	-0.638
O2 - carbonyl	-0.764	-0.628	-0.691	-0.905
O3- phenolic	-0.727	-0.708	-0.753	0.776

H2O5: N,3-dihydroxy-2-naphthamide; SHA: salicylhydroxamic acid.
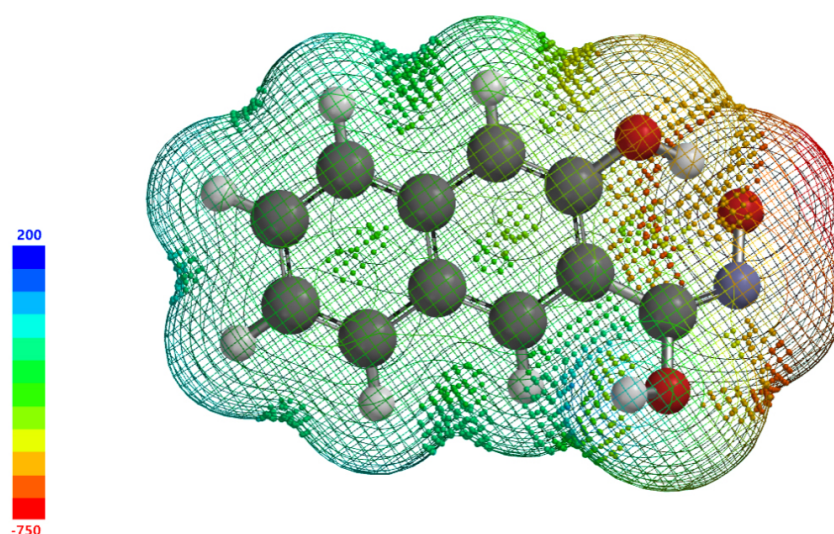
**Figure 6.** H2O5 enol E anion electrostatic potential map. H2O5: N,3-dihydroxy-2-naphthamide.

Particle size distributions show that the P80 for the 10-min grinding time was approximately 110 ± 25 µm over the four experiments, for the 14.5-min grinding time was approximately 85 ± 16 µm over the three experiments, and for the 19-min grinding time was approximately 68 ± 8 µm over the 22 experiments. REM recovery as a function of grind time is shown in Figure 9 from the published[32] work.

The plot shows that recovery increases as milling time increases. REM recovery increases as the grind time increases, as seen in the trend for the SHA experiments at 333.3 g/tonne, due to decreased particle size. The recovery of REMs for the two SHA experimental designs and the H2O5 experimental design at 19.0 min of grind time is shown in Figure 10.

The experiments for SHA at 83.3 and 416.7 g/tonne are at the non-optimal pH of 6 and 9 which are a part of the unpublished SHA experiments along with the SHA at 250.0 g/tonne. This experimental design identified the optimal pH for REM flotation using SHA as 7.5 which can be observed in the published SHA experiments at 333.3 g/tonne having a higher REM recovery at the same pH (7.5) and milling time (19 min)

-17.9518

-630.279
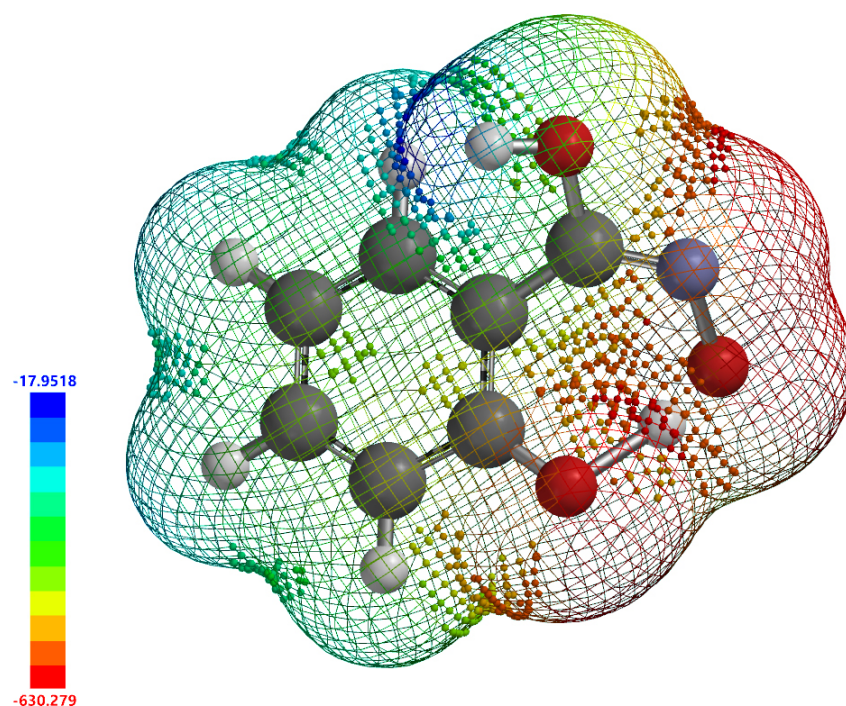
Figure 7. SHA enol E anion electrostatic potential map. SHA: Salicylhydroxamic acid.
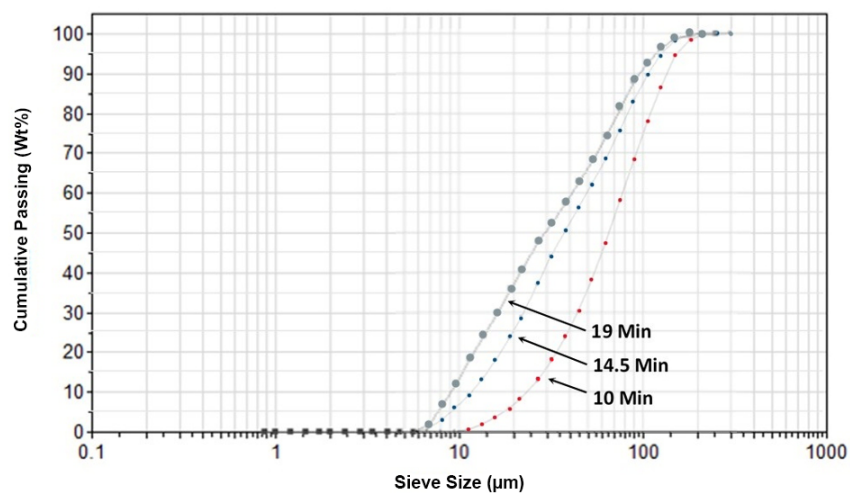
Figure 8. Particle size distributions as determined from mineral liberation analysis for flotation feed experiments at 10, 14.5, and 19 min of milling time.

as the 250.0 g/tonne SHA experiments. The highest SHA REM recovery, 70.4%, was at 750.0 g/tonne and a pH of 7.5. H_2O_5 has a higher REM recovery than the SHA, with the highest recovery observed at a pH of 11 and 750.0 g/tonne of 86.6%, which is approximately a 23% increase. Fit statistics for the three experimental design models and model *P*-values from the analysis of variance are shown in Table 5.

Significant models were developed for all three experimental designs, with the unpublished SHA experiments having the highest *P*-value but still below the traditional 0.05 (or 95% confidence) to define

Table 5. Fit statistics and analysis of variance *P*-value for the three experimental designs (model *P*-values are significant as determined from analysis of variance)

Collector	Model *P*-value	Std. Dev.	Mean	C.V. %	R^2	Adj. R^2	Pred. R^2
Published SHA	0.0007	3.78	57.43	6.59	0.7818	0.7546	0.6005
Unpublished SHA	0.0184	3.33	42.95	7.75	0.6806	0.5894	0.2283
H2O5	0.0008	1.25	80.14	1.56	0.9554	0.9442	0.8642

SHA: Salicylhydroxamic acid; H2O5: N,3-dihydroxy-2-naphthamide.
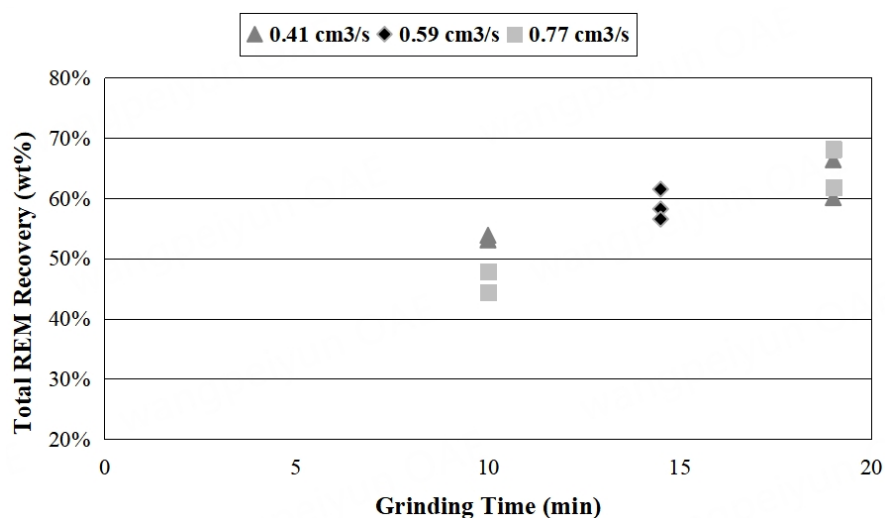
Figure 9. Rare Earth Mineral flotation recovery utilizing SHA *vs.* milling time. The plotted points are grouped by the superficial gas velocity. See Table 5 and associated discussions for statistical analyses. SHA: Salicylhydroxamic acid.
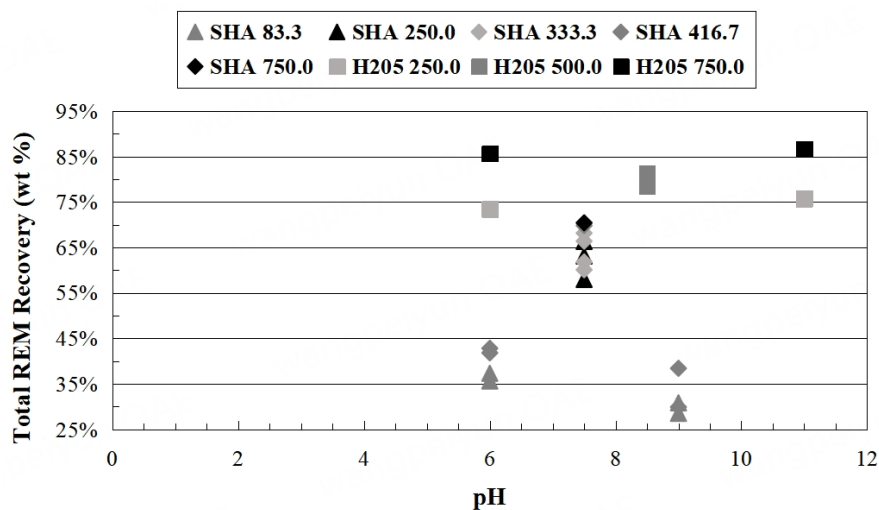
Figure 10. Comparison of the effect of collectors on the recovery of rare earth minerals by flotation. The comparison is between SHA and H2O5 from three sets of experimental designs. At similar dosages, H2O5 had a higher recovery than SHA. See Table 5 and associated discussions for statistical analyses. SHA: Salicylhydroxamic acid; H2O5: N,3-dihydroxy-2-naphthamide.

significance. All three models also had a lack of fit that was not significant, which implies that the data fits the model. The coefficient of variation (C.V. %) is below 10% for all the models, which implies that the data

is relatively precise and is likely reproducible. R^2, Adjusted R^2, and Predicted R^2 for the H2O5 approach one, which signifies that the experimental data matches the predicted model; the correlation is normalized for the number of samples and still matches the experimental data, and the model is expected to be able to predict new values for experiments for design points that have not been performed within the design space. The degree of confidence in the published SHA and unpublished SHA models is less, but they still can be used for comparison purposes. However, the models should not be used to predict behavior.

CONCLUSIONS

From the FT-IR (H-NMR, and LRS) spectral data, it was shown that the collector H2O5 was successfully synthesized from BON acid and that, as expected, it was similar to SHA, its analog. Clearly, the synthesis procedure can be used for necessary future work on this collector, particularly with respect to REM flotation. Upon complexation with Cu^{2+}, the characteristic carbonyl (C=O) peak and amine (N–H) vibrations became significantly depressed, whereas amide (C=N) became prominent. These results suggest that the HAs complex with metal via Keto-Z and Enol-Z tautomerization, which causes the carbonyl oxygen to become more electronegative. According to coordination chemistry theory, this allows oxygen to donate free valances to metal ions, suggesting that the Enol-Z form is preferred as needed to maximize chelation bonding of both H2O5 and SHA, which is common for HA collectors. Spartan modeling and flotation testing suggest H2O5 is a better collector, yielding higher recoveries by 23% than SHA.

A more detailed study is still needed to investigate the adsorption behavior of H2O5 and determination of a route to increase the yield during synthesis. This work should include a comprehensive study on the surface properties, including zeta potential and full adsorption isotherms, to understand surface area and other related studies. Additionally, work needs to be performed to develop a more complete optimization of rare earth mineral flotation using H2O5 such as determining the optimal pH and reagent dosage and investigating if column flotation is more appropriate given the small grain sizes of the rare earth mineral to achieve liberation.

DECLARATIONS

Authors' contributions
Made substantial contributions to the conception and design of the study and performed data analysis and interpretation: Suslavich B, LaDouceur R, Young C
Performed data acquisition and provided administrative, technical, and material support: Suslavich B, LaDouceur R, Young C
Helped with the editing of text and figures: Suslavich B, Mamudu A

Availability of data and materials
Most data can be found in the dissertation by LaDouceur R, Montana Tech, Butte MT (2017), but we decided not to reference that in this article because the data has been evaluated differently per the review process.

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Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
Not applicable.

Consent for Publication
Not applicable.

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