



Milestone towards the Commercialization of Ion Flotation for Rare Earth Elements Recovery and Purification

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Abstract:

In this work, the results of foam flotation of La (III), Ce (III) and Nd (III) ions individually, as a group, and as a group with gangue ion Ca (II) are reported. The ion flotation was investigated using anionic surfactants—sodium dodecyl sulfate (SDS) which having the ability to form complexes with metal ions. Foam (ion and precipitate) flotation is a promising green method for the recovery of rare earth elements (REE). It was found that the floatability of REE with SDS depends considerably on the composition of the REE solution and demonstrate that the recovery kinetics can be used as an additional control of the REE separation in the group flotation with gangue ion. Overall, the work results demonstrate that foam flotation is capable of selectively recovering an individual REE from a mixture of several REE with gangue ion, provided that the flotation conditions such as surfactant concentration, solution pH and flotation time are properly selected. The best results were obtained for single-ion flotation, SDS concentration was 0.75 mM, initial concentrations of REE was 0.3–0.35 mM, REE: SDS molar ratio of 1:2 and pH 7 for Nd (III), pH 9 for La (III) and for Ce (III) very high recovery at the 1:2 ratio at pH 7 and additional ratio of 1:3 at pH 3 at 90-180 min flotation time respectively. While in the group flotation are presented in La (III) 0.36 mM, Ce (III) 0.36 Mm and Nd (III) 0.32 mM, SDS concentration was 0.7 Mm, the total REE: SDS molar ratio in group flotation was 2:1, and pH 7 at 30-70 min flotation time respectively. For group flotation with gangue ion, the initial concentrations of REE and gangue ion are presented in La (III) 0.54 mM, Ce (III) 0.9 mM, Nd (III) 0.1 mM, Ca (II) 2.5 mM, SDS 0.75 mM and pH 3 at 90 min flotation time respectively. These results are an important milestone toward the commercialization of foam flotation for the recovery and purification of REE.

KEYWORDS: Ion Flotation, Rare Earth, Recovery, Purification, Commercialization

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I. Introduction

The rare earth elements (REEs) are a series of elements with similar physicochemical properties which includes 15 elements of lanthanides and scandium, yttrium. The industrial applications of these elements have been extended to metallurgy, magnets, ceramics, electronics, chemical, optical, medical, agriculture and nuclear technologies in the past century owing to their unique properties⁽¹⁻⁴⁾. At present, REEs are mainly produced from bastnasite, monazite, ion-absorbed clay, xenotime and loparite⁽⁵⁻¹¹⁾. However, the increasing demand, especially from green energy and new materials⁽¹¹⁻¹⁵⁾ exacerbated its contradiction with the shrinking easy-processing REEs resources. Which makes the exploration of new origins of REEs become an urgent subject, especially for heavy rare earth elements (HREEs)⁽¹⁶⁻¹⁸⁾. So far, efforts for sustainable development of REEs resources have been paid on following aspects: (1) Recycle REEs from manufacturing rare earth scrap/residues⁽¹⁹⁾; (2) Reclaim REEs from End-of-Life products⁽²⁰⁻²²⁾; (3) Extract REEs from landfill mining of industrial wastes or residues⁽²³⁻²⁶⁾. While, up to now, most of them are limited to academic research due to the difficulties of collection, technique and economy^(19,27). Besides, an enormous amount of research has focused on (4) REEs recovery from trace REEs associated minerals such as uranium (U) ore⁽²⁸⁾, fluorite⁽²⁹⁾, sea sediments^(30,31), and phosphate rocks⁽³²⁾, etc.

The available technologies of the REE separation (ore/froth flotation, solvent extraction, precipitation, adsorption, and ion-exchange) are economically uncompetitive, highly energy and water demanding, and highly polluting⁽³³⁻³⁵⁾. In particular, solvent extraction is typically used for separating individual REE recovered in the primary step by froth flotation or precipitation⁽³⁵⁾. The solvent extraction process is generally constituted of hundreds of stages where hazardous organic solvents and toxic extractants such as di-(2-ethylhexyl) phosphoric acid are used⁽³³⁾. A special challenge of the available methods is to separate heavy REE (Tb to Lu) because they

are present in a more dispersed form in the ore bodies as compared to light REE (La to Gd) ⁽³⁶⁾. Addressing this challenge places additional energy, water, cost, and industrial space penalties on the REE separation technology.

A greener alternative to the conventional REE extraction and purification methods can be and precipitate flotation ⁽³⁷⁾. In ion flotation, target ions adsorb on the headgroups of surfactant films that stabilize bubbles dispersed in the solution. In precipitate flotation, target ions attach to these bubbles as precipitates with or without surfactants. The loaded bubbles rise to the top of the cell where they are collected as a foam. Like froth flotation, both ion and precipitate flotation employ surfactants as collectors and rely on bubbles and gravity, but instead of dispersed mineral particles, they separate dissolved ions from their mixture. It can be difficult to differentiate a priori ion and precipitate flotation from each other in practice. Therefore, we collectively call these two flotation processes ‘foam’ flotation ⁽³⁷⁾ to distinguish them from froth flotation and foam fractionation. The former term is currently associated with ore flotation while the latter is commonly used for a foam-based process that separates soluble organic species.

When compared to solvent extraction, foam flotation offers several important advantages including lower water consumption, facile and flexible operation, lower energy consumption, lower sludge, lower operational costs, and no toxic or hazardous organic chemicals and solvents ⁽³⁸⁻³⁹⁾. In contrast to the solvent extraction, foam flotation can be applied to a wide range of ion concentrations, while the used surfactants and water can be recovered from the foam flotation product and recycled ⁽⁴⁰⁻⁴¹⁾.

So far, foam flotation has widely been applied to the removal of toxic heavy metal ions from wastewater, while separation of REE is much less explored ⁽³⁷⁻³⁸⁾. Though the paradigm of foam flotation of metal ions in general, and REE, in particular, is still emerging, there is consensus that the selectivity of foam flotation strongly depends on the valency charge and the solution pH ⁽⁴²⁻⁴³⁾. Specifically, selectivity toward a target metal ion in group flotation increases with an increase in the valency of this ion ⁽⁴²⁾. pH affects the hydrolysis state of dissolved multivalence cations and hence their complexation and precipitation with anionic collectors ⁽⁴⁴⁻⁴⁶⁾. This effect has been employed by Sawaji et al. (1992), to separate individual REE based purely on pH using phosphonic acid collectors ⁽⁴⁴⁾. However, their scheme was based on the single-ion flotation. Another complication of the separation scheme proposed by Sawaji et al. (1992) is that at high pH soluble anionic metal complexes were formed, which led to a drop in the recovery of all REE ions except for Nd and Sm.

Our work demonstrates the effect of pH concentration and surface tension on the foaming effect of the selected REEs compared to their group including the impurity ion, we selected three light chemical elements (La, Ce and Nd). Being a conventional surfactant, SDS is by far the most commonly used conventional surfactant ⁽⁴⁷⁻⁵⁰⁾.

II. Experimental

II.1. Materials and Methods:

Sodium dodecyl sulfate (SDS) high purity, La (NO₃)₃·6H₂O (99.9%), Ce (NO₃)₃·6H₂O (99.5%), Nd (NO₃)₃·6H₂O (99.9%), CaCl₂ (99%), were obtained from Sigma Aldrich, Arsenazo (III) (pure, Sigma chem. C. O. USA). Critical micelle concentrations (CMC) of SDS provided by the manufacturers are 7–10 mM. REE solutions were prepared from their nitrate. The pH- values of the solutions were measured using pH meter model 3510, Jenway, England, was adjusted using NaOH (99.9% pellets) and HNO₃ (70 wt %), obtained from Sigma Aldrich. 0.1 M NaNO₃ was used as a background electrolyte. The initial concentrations of SDS were 0.75–1 mM. The initial collector concentrations were set below CMC to maintain high collector efficiency and minimize the surfactant consumption. The molar ratio of REE to surfactant was set to 1:2 in all but one study (in group flotation, the 1:2 ratio applies to the concentration of each REE to the total SDS concentration). The initial concentrations of REE and gangue ion in the group flotation are presented in La (III) 0.36, 0.54 mM, Ce (III) 0.36, 0.9 mM, Nd (III) 0.32, 0.1 mM, Ca (II) 2.5 mM.

II.2. Foam flotation:

Ion Flotation Machine is shown in Figure (1). The air flow was controlled at 7–10 mL/min., A glass frit with a pore size of 10–15 μm was used to generate small bubbles and stable foam. In all the foam flotation experiments, the volume of the flotation feed solution was 150 mL for SDS. The foam exit height (the distance between the surface of the solution and the exit port) was set at 50 mm for SDS solution.

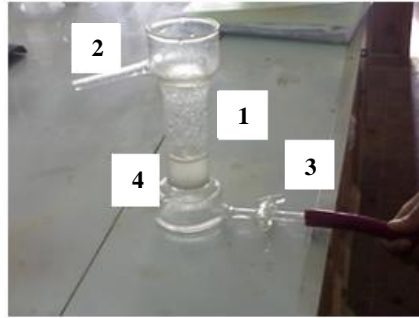


Figure (1): A schematic view of the Flotation Cell, (1)200 mL flotation cell, (2) A stopper to capture foam, (3) A stopcock with an airspeed of 7–10 mL/min, (4) Frit with a pore size of 10–15 μm .

A pH meter was used to measure the pH of the feed and tailing solutions before and after each experiment, respectively. The foam was collected for an average of 120 min. each using a measuring cylinder. The results of foam flotation were analyzed using the recovery and distribution factors.

Recovery factor (%R) is defined as a ratio of the amount of target ions recovered into the foamate (collapsed collected foam) to the initial amount of these ions in the feed ⁽⁵⁰⁾:

$$\%R = \left(\frac{V_{\text{foamate}} C_{\text{foamate}}}{V_i C_i} \right) \times 100$$

where V_{foamate} and V_i are the volumes of the foamate and initial (feed) solution, respectively in liters, and C_{foamate} and C_i are the concentration of the metal ion in the foamate and initial feed solution in mg/L, respectively.

The distribution factor (D) is defined as the concentration ratio of the targeted metal ion in the foamate to the tailings ⁽⁵²⁾:

$$D = \left(\frac{C_{\text{foamate}}}{C_t} \right)$$

where C_{foamate} and C_t are the concentrations of the target ion in the foamate and the tailing solution. In the case of a single REE flotation, D measures the enrichment of the REE in the foam vs the tailing, which characterizes the affinity of the surfactant to the REE. In the case of multiple ions, D characterizes the flotation selectivity toward a target ion.

Concentration of total REE was analyzed using a double beam of UV-Vis spectrophotometer model Jasco V-530 with a wavelength (650 nm) using Arsenazo (III) method and Nd (III) by direct spectra were measured at (521nm), Ce (III) were determined by titration method using Cerium Sulfate(0.02M) and ferroin as indicator.

III. Results and Discussion

The results of single REE ion solution, group REEs (La (III), Ce (III) and Nd (III)) ion solution with SDS collector and group (La (III), Ce (III) and Nd (III)) with gangue (Ca (II)) will be demonstrated with their discussions successively during the following:

3.1. Single REE ion flotation:

Foam flotation of individual REE ions from their single-ion solutions in 0.1 M NaNO_3 with SDS as a collector was carried out to understand the effect of pH. The solution pH was varied from 3 to 7–9. These concentrations correspond to the REE: SDS molar ratio of 1:2. The recovery and distribution factor of REE with SDS are shown in Figure (1). As seen from Figure (2a), the recovery of all the REE tested increased with the increasing pH. The recoveries of Ce (III) and La (III) were moderate at low pH (<4), and remained nearly constant at intermediate pH (4–6). At pH 7 for Ce (III) and at pH 9 for La (III), it was observed a precipitation as well as a step increase in the recovery. Based on the earlier work, this increase in the recovery was attributed to the precipitation of $\text{La (III)(OH)}_x(\text{SDS})_y$ and $\text{Ce (III)(OH)}_x(\text{SDS})_y$ complexes ⁽⁵³⁻⁵⁶⁾.

In contrast, the increase in the recovery of Nd (III) with pH was relatively gradual. This effect can be explained by both ion and precipitate flotation which is controlled by pH and SDS concentration. Figure (2), also shows that both the recovery and distribution factor were at significant but moderate values (~48% and 10 times, respectively) for Ce (III) even at acidic condition (pH ~ 3) where the hydroxylation of Ce (III) is least

avored. This result is new because the prior literature concluded that recovery of REE is highly favored only at pH values where precipitation/hydroxylation starts appearing^(53- 57). For Ce (III), these studies observed that better flotation occurred at pH 5.5 or above. For pH below 5.5, they found a negligible recovery for Ce (III). They hypothesized that a lack of metal hydroxyl complex formation at these low pH values to be the reason for such poor recovery of Ce (III). We believe that this discrepancy with our results (moderate recovery of Ce (III) at low pH) is due to the lower concentration of SDS that was used in their studies (0.3 mM.). It is well known that the hydroxylation and formation of soluble polynuclear La (III) complex is possible at acidic pH through an olation process Figure (3),⁽⁵⁸⁻⁵⁹⁾. It is suggested that at high SDS concentrations this process can lead to precipitation of the polynuclear La (III) - SDS complex.

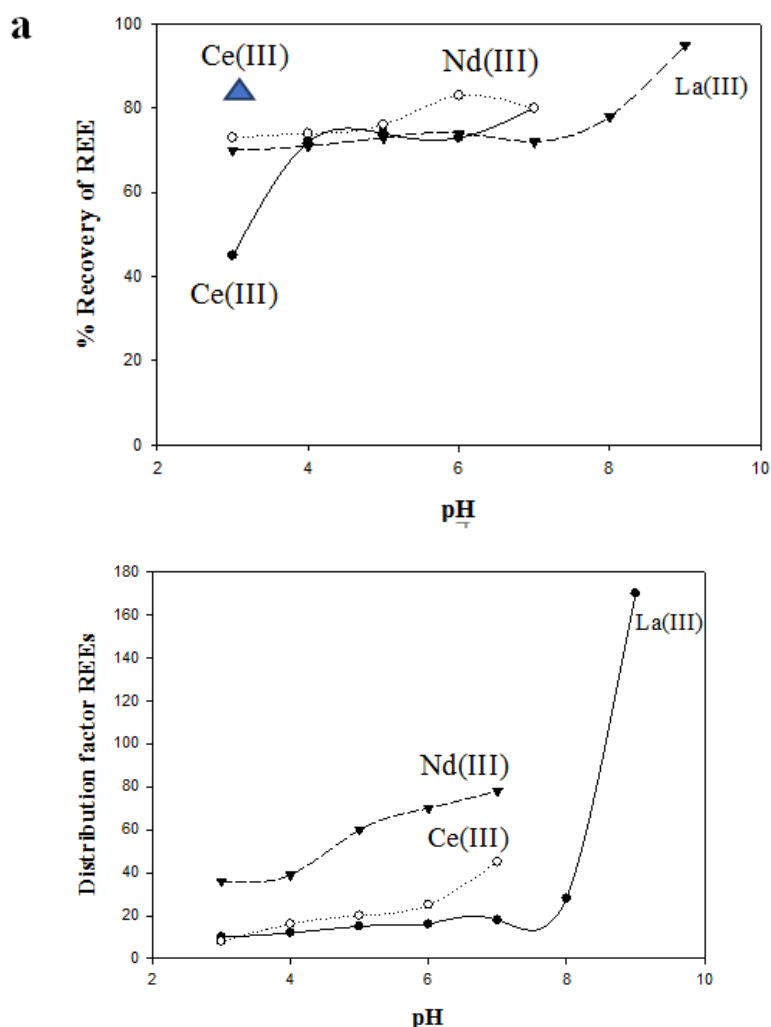


Figure (2): Effect of pH on foam flotation of individual REE by SDS in a 0.1 M NaNO₃ solution at REE: SDS concentration ratio of 1:2 (for Ce (III), an additional ratio of 1:3 was tested at pH 3), (a) recovery and (b) distribution factor of REE. The initial concentration of REE and SDS is 0.3–0.35 mM and 0.75 mM., respectively, 90–180 min flotation time.

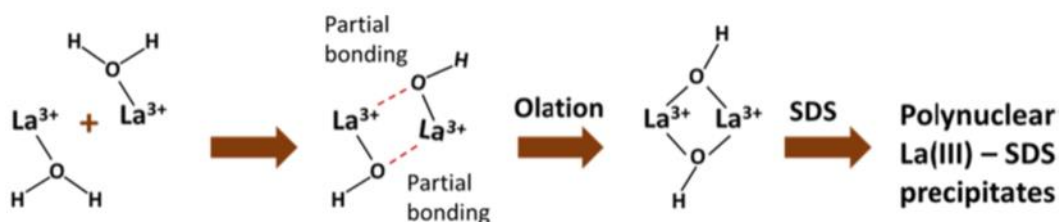


Figure (3): Hydrolysis, olation, and precipitation process of polynuclear aqua lanthanide ion in the presence of SDS.

To understand the effect of the SDS concentration, foam flotation of Ce (III) at two different REE:SDS ratio (1:2 and 1:3 M ratio with SDS concentration at 0.75 mM and 1 mM respectively) at pH 3 was tested. As seen from Figure (2a), at the REE:SDS ratio of 1:3, a recovery of 95% Ce resulted in simultaneous appearance of Ce (III)-SDS precipitates. This recovery is much higher than the 48% recovery was observed for REE: SDS of 1:2 under the same conditions. At the same time, the recovered foam at 1:3 ratio was wetter than at 1:2, resulting in three times larger foam volume. An increased recovery of Ce with increasing SDS concentration implies that the precipitates that we observed are due to metal ion-SDS complex and the flotation process could lead the hydroxylation of metal-ions at this low pH. The observed wetter foam at a 1:3 ratio is also consistent with an earlier work of foam flotation of heavy metal ions with SDS ⁽⁶⁰⁾. This work showed that a high recovery ensued at a 1:3 ratio but also resulted in a poor enrichment. Hence, it was suggested that optimum concentration of the surfactant is critically tied to the foam flotation pH and a higher surfactant concentration can potentially lead to poor selectivity in the case of multiple-ion flotation. Based on the moderate recoveries at low pH at the 1:2 ratio and very high recovery at the 1:3 ratio (with the concomitant appearance of precipitates), it was concluded that both ion and precipitate routes of foam flotation can be activated and the recoveries and selectivity can be controlled using pH and SDS concentration as variables.

3.2. REE group flotation :

In this section, the effect of other REE ions on the foam flotation of a target REE ion is reported. In particular, the foam flotation of three REE ions (La (III), Ce (III) and Nd (III) as a group was carried out at a total REE: SDS molar ratio of 2:1 at different pH. Remarkably, the pH dependent behavior of the recovery and the distribution factor (selectivity) is different when an REE is floated in a group Figure (4 and 5) as compared to single-ion flotation Figure (2). The recoveries of both La (III) and Ce (III) were significantly lower than the corresponding recoveries from single-ion flotation at the entire pH range studied (3.2–7.2). For example, at pH 7.2, La (III) and Ce (III) in the group flotation showed recoveries of 48% and 55%, respectively, whereas, corresponding recoveries in single-ion flotation were 72% and 80%. On the other hand, the recoveries of Nd (III) in group flotation were lower than even La (III) and Ce (III) at low pH range (3.2–6.2) but shows considerably higher recoveries and hence selectivity at high pH (recoveries of ~ 80% at pH 7.2 for Nd (III)).

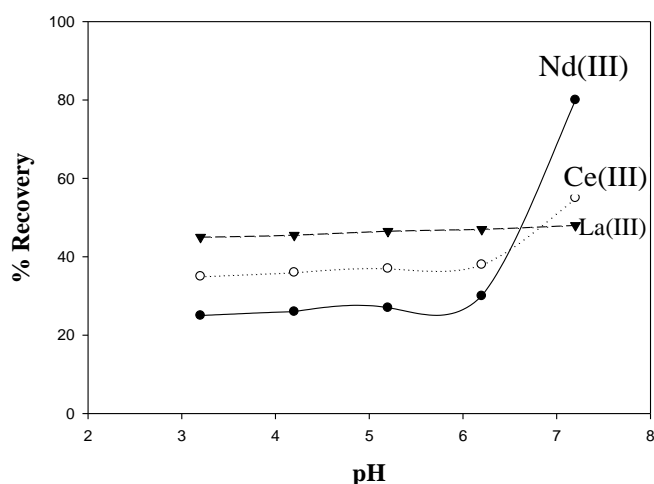


Figure (4): Effect of pH on the selective recovery of La (III), Ce (III) and Nd (III) in their group foam flotation by SDS. The initial total REE: SDS molar ratio was set at 2:1 (initial concentrations of REE is (La (III) 0.36 mM, Ce (III) 0.36 mM, Nd (III) 0.32 mM) and SDS is 0.7 mM) and 0.1 M NaNO₃ is used as a background electrolyte.

The above results suggest that both La (III) and Ce (III) are recovered well by the ion flotation route at low and circumneutral pH (since no precipitates were observed) as compared to Nd (III). Whereas, at basic pH value (where precipitation of REE was noted), the opposite behavior is observed, i.e., Nd (III) was recovered better than La (III) and Ce (III). Thus, at low SDS concentrations when the REE ions compete for SDS, a clear differentiation of foam flotation mechanism can be achieved by controlling the pH, i.e., ion- and precipitate-flotation at low and high pH, respectively.

The distribution factor reveals interesting trends Figure (5) between single-ion and group flotation recovery of REE ions. At acidic and circumneutral pH, the distribution factor of all REE ions (except La (III)) in the group flotation was lower than the single-ion flotation values. In the case of La (III), the effect of the presence of other REE ions had a minimal impact on the pH values as high 7.2. The distribution factor of Ce

(III) and Nd (III) factor increased gradually up to pH ~ 6.2 pH and experienced a sudden increase at pH 7.2. All the earlier study on foam flotation of REE ion were always restricted to single ion or two ions' solutions (Chirkst et al., 2009a; Micheau et al., 2015; Lobacheva et al., 2013; Chirkst et al., 2011; Lobacheva et al., 2014b). These limited studies posited that the separation of REE elements can be achieved by foam flotation at various pH (Chirkst et al., 2009b; Chang et al., 2019). The results show that recovery Figure (4) and the distribution factor Figure (5) of an REE ion in group flotation was drastically different from the single-ion flotation results. It is clear that even in acidic condition flotation of ions are possible which contradicts the literature (Chirkst et al., 2009b; Chirkst et al., 2011). Hence, any pH-based separation scheme must be formulated based on the group-flotation results with multiple REE ions. Since the foam flotation is adynamic(non-equilibrium) process, it is important to optimize the flotation time. Hence, the recovery of REE as a function of flotation time Figure (6) using the group foam flotation with the three REE ions (La (III), Ce (III) and Nd (III)) was examined. The initial SDS: REE and pH were kept at 1:2 and 7, respectively, and the foams were collected at regular intervals. In the first 30 min, the Nd (III) was recovered at 41% and followed by Ce (18%), and La (14%), it is the first report of the kinetics of the REE recovery in the presence of multiple REE ions.

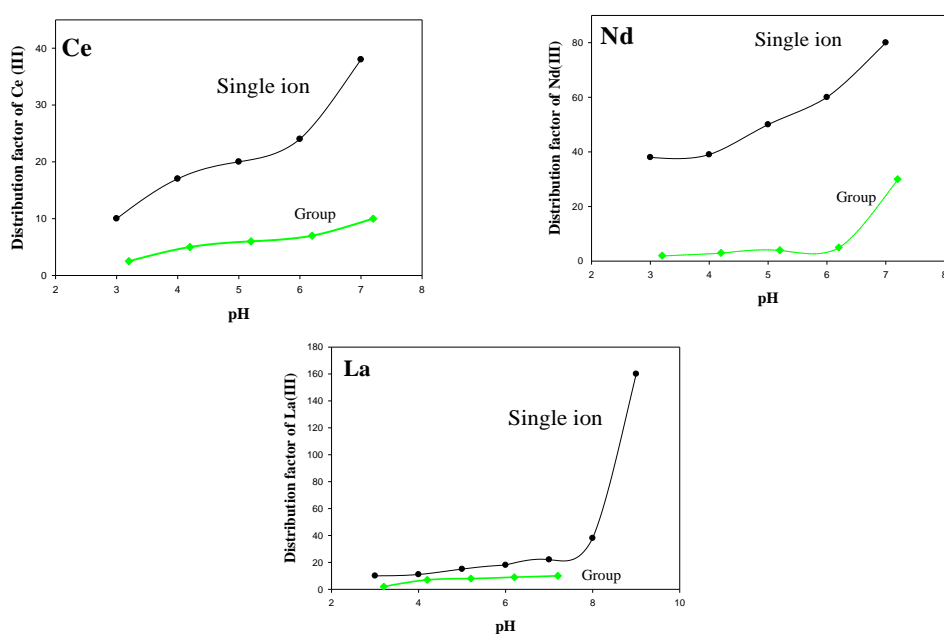


Figure (5): Effect of pH on the distribution factor of Ce (III), Nd (III) and La (III) in group foam flotation by SDS. The group-flotation (green squares) is compared with single-ion flotation (black circles). The initial concentrations of REE in group flotation is given in the above and the SDS is 0.7 mM; the total REE: SDS molar ratio in group flotation was 2:1. 0.1 M NaNO₃ was used as the background electrolyte.

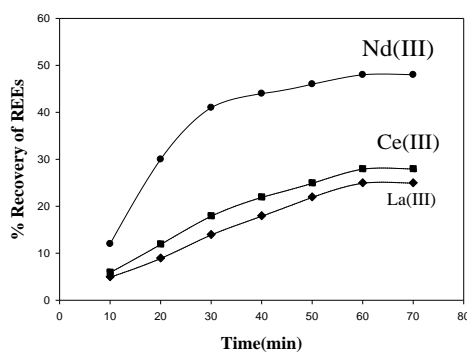


Figure (6): Kinetics of the group foam flotation of La (III), Ce (III) and Nd (III) with SDS at pH 7 at the REE: SDS molar ratio of 2:1. The initial concentration of REE is given in the above and the initial concentration of SDS is 0.7 mM.

3.3. REE group flotation with gangue ion:

To study the effect of gangue on foam flotation of REE, group flotation with 0.75 mM SDS of the three REE (La (III) 0.54mM, Ce (III) 0.9mM, Nd (III) 0.1mM) in the presence of gangue ion Ca (II) 2.5mM at pH 3.6. The choice the acidic pH since we observed high precipitation at pH 5.5 and above (likely due to gangue ion). The recovery of REE and gangue ion at different time intervals are shown in Figure (7). The final recovery of all the REE was similar (57%-67%), whereas the recovery of gangue ion was poorer (< 10%). Overall, it can be concluded that SDS shows higher selectivity towards REE compared to gangue ion, which has important practical implications. Another important finding is that REE ions preferentially report to the foam by the time it started collecting the foam at 9th minute, at which point no gangue were detected in the foam. Only after 20 min, it was noticed a trace quantity of gangue reporting to foam. This suggests that careful control of kinetics can allow a selective and efficient separation of REE from gangue, which can make economical a simple multistage foam flotation-based separation of REE.

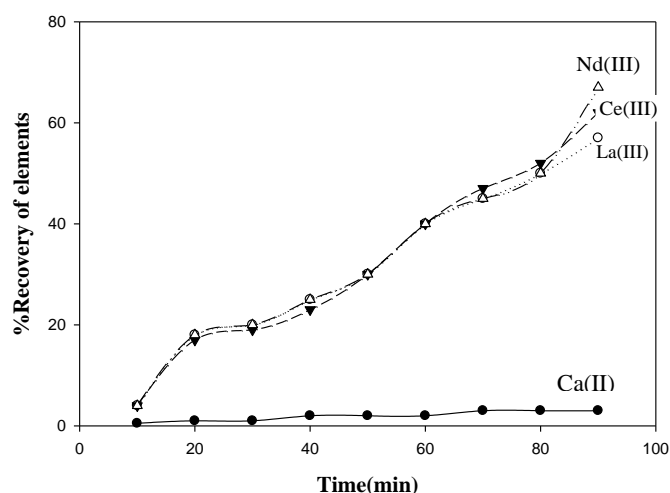


Figure (7): Recovery (%) with time of group flotation (La (III) 0.54mM, Ce (III) 0.9mM, Nd (III) 0.1mM) by SDS (0.75 mM) in the presence of gangue ion Ca (II) 2.5mM, at pH 3.6 in 0.1 M NaNO₃.

IV. Conclusions

Foam flotation of REE in single-ion, group was carried out using SDS as anionic collectors. We find : (a) The pH dependence of the single-ion flotation of Nd (III), Ce (III), and La (III) by SDS suggests two different mechanisms of the REE recovery—ion flotation and precipitate flotation dominated at low and high pH, respectively. Precipitate flotation can be activated even at lower pH by SDS at higher concentrations. (b) The recovery of REE decreases in the following order: single-ion flotation (SDS) > group flotation (SDS) > group flotation with gangue (SDS). (c) REE were more selectively floated at acidic pH (d) In the group flotation with gangue ion by SDS, the REE were recovered faster compared to gangue. These results indicate that foam flotation can selectively separate REE against each other as well as against gangue ion.

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