

THE METHOD OF REMOVAL YTTRIUM (III) AND YTTERBIUM (III) FROM DILUTE AQUEOUS SOLUTIONS

Olga Lobacheva¹, Natalia Dzhevaga¹, Aleksandr Danilov¹

¹ National Mineral Resources University (Mining University), Vasil'evsky Island, 21 line 2, Saint-Petersburg, 199106 Russia, e-mail: olga-59@yandex.ru, dzhevaga331@mail.ru, twixsek@mail.ru

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ABSTRACT

Yttrium (III) and ytterbium (III) cations ion flotation from diluted aqueous solutions in the presence of chloride ions using sodium dodecyl sulfate as collector agent were studied. Y (III) and Yb (III) distribution and recovery coefficients as a function of aqueous phase pH value at different sodium chloride concentrations were received. Yttrium (III) and ytterbium (III) chloro and hydroxo complexes instability constants were calculated. The calculation of separation coefficient at pH specified values depending on chloride ion concentration was conducted. Maximum separation coefficient was observed when chloride concentration of 0.01 M is 50 at pH 7.8. K_{sep} is minimal in nitrate medium and is 3 at pH 7.0. At sodium chloride concentration of 0.05 M K_{sep} is 9 at pH 7.8.

Keywords: ion flotation, sodium dodecyl sulfate, distribution coefficient, separation coefficient, removal.

INTRODUCTION

Ion flotation is a process based on adsorption at liquid-gas phase boundary of surfactant and inorganic compound ions reaction products. The method is widely used for recovering substances from solutions with concentrations of $10^{-2} - 10^{-8}$ mol/l. Ion flotation is based on recovering ion attraction by oppositely charged collector ions that had attached to the surface of air or gas bubbles that are let through the solution [Gol'man 1982]. Various classes of surfactants are used as collector agents. Ion flotation method permits recovering non-ferrous, rare-earth and heavy metal cations from diluted aqueous solutions and industrial waste waters.

Rare-earth elements are widely used in different branches of industry. Thus lanthanum, cerium and yttrium are used for manufacturing glass, ceramics, catalysts; samarium is used while manufacturing magnets and lasers; europium is used when manufacturing luminophor; holmium and erbium are used when manufacturing ceramics and in nuclear industry. It should be noted that

all Russian rare-earth deposits are part of complex deposits, whose processing does not include recovering rare-earth elements. For example, a joint-stock company 'Apatite' is a large mining complex whose sphere of activity are booty and enriching of apatite-nephelites ores of Hibiny deposits, production apatite and nephelite concentrates, and also other mineral concentrates – syenite, titanium magnetite. A nephelite concentrate containing no less than 28,5 percent of Al_2O_3 is used for the production of aluminum, soda, potash, cement, phosphoric-potassium fertilizers, coagulants of containing an aluminium, brick wares, glass wares, rare-earth elements, different salts of aluminium and other foods outside a joint-stock company 'Apatite' [Danilov et al. 2015].

Multipurpose use of mineral raw materials is the most important direction for resource-saving in new millennium. Separated pure rare-earth elements have extrinsic value. That is why an increase in efficiency of separation of rare-earth elements with similar properties is a pressing problem, permitting decreasing the cost of individual rare-earth elements and their oxides, and expand

the possibility of their use. When employing ion flotation high separation factors for rare-earth elements are not observed [Chirkst et al. 2009a]. Studying of chloride ions influence on ion flotation process is of interest.

MATERIALS AND METHODS

Ion flotation process was conducted in mark 137 V-FL laboratory flotation machine with a cell of 1 dm³ for 5 minutes. Chemically pure 0.001 mol/l yttrium and ytterbium nitrates solutions were used as standard test solutions. Solution volume was 200 ml. Dry sodium dodecyl sulfate combining both collector and foaming agent properties with general formula C₁₂H₂₅OSO₃Na was used as a surfactant. Its concentration conformed to stoichiometry of the following reaction:



i.e. it is 0.003 M (DS⁻ – dodecyl sulfate ion). Sodium chloride was also added to initial solution at a rate corresponding to the concentration of 0.01 and 0.05 mol/l. The received froth and chamber products were separated and analyzed. The froth was destroyed by using 1 M sulphuric acid. Rare-earth elements concentration was determined by photometric method with arsenazo III [Savin 1966]; chloride ions concentration – by mercurimetric titration method with mixed indicator (0.5 mass % of diphenylcarbazide alcohol solution and 0.05 mass % of bromphenol blue) [Kresh-

kov 1976]; dodecyl sulfate ion concentration – by potentiometric titration method by 0.002 M cetyltrimethylammonium chloride solution with ion-selective electrode, consisting of silver-chloride-EVL-1M3, put into NaDS and NaCl solution, and membrane, selective to DS⁻ ion. The membrane was manufactured by Ionometry Laboratory of St. Petersburg State University Department of Physical Chemistry [Timofeev et al. 1978]. The value of pH solutions pH value ranges from 4 to 9 in increments of 0.5 and adjusted by nitric acid or sodium hydroxide solution.

Metals cations distribution coefficients between froth and chamber products were calculated by [Me³⁺] concentration in the froth product relative to [Me³⁺] concentration in chamber residue in accordance with formula [Zolotov 2004]:

$$D = \frac{C_{org}}{C_{aq}} \quad (2)$$

and separation coefficient

$$K_{\text{Me}_1/\text{Me}_2} = \frac{D_{\text{Me}_1}}{D_{\text{Me}_2}} \quad (3)$$

In Figures 1 and 2 distribution coefficients as a function of pH at different sodium chloride concentrations for yttrium and ytterbium cations are shown.

When flotating yttrium (III) cations in acidic medium at NaCl concentration of 0.01 M in the range of pH < 6.7 the recovery is near zero. The abrupt jump of K_{distr} is observed at pH 6.7. Max.

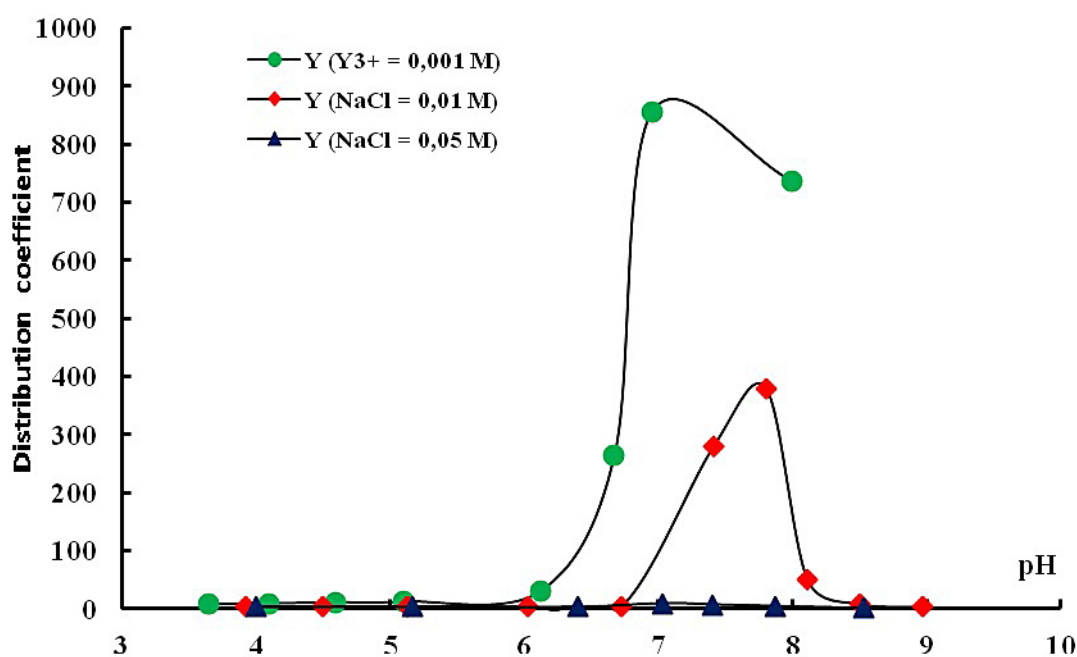


Figure 1. Yttrium K_{distr.} as a function of pH at different chloride concentrations

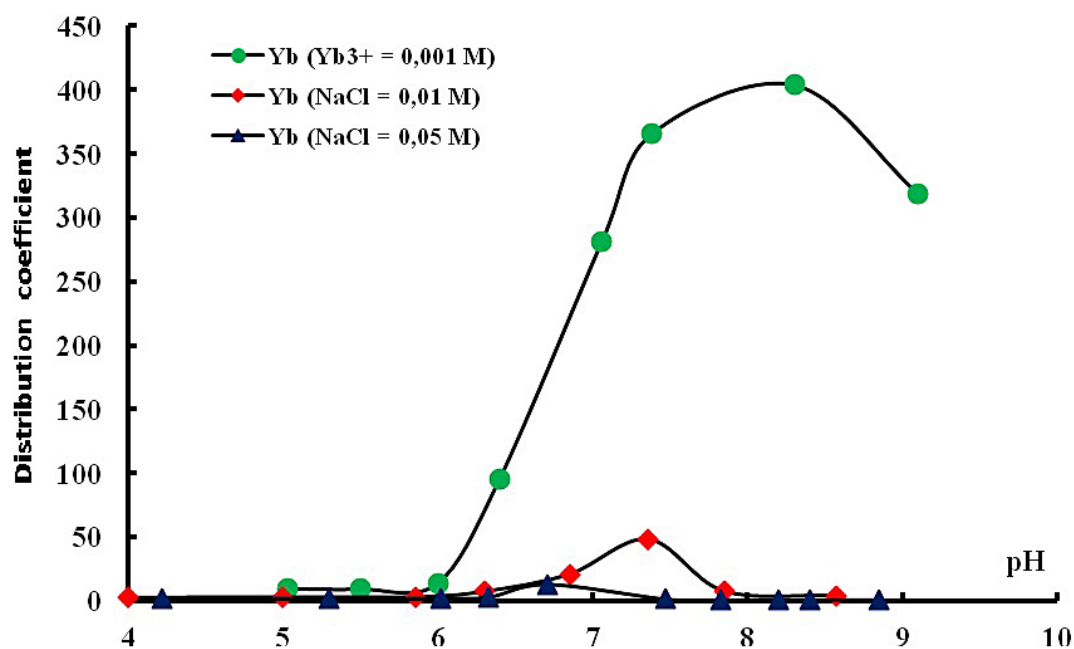


Figure 2. Ytterbium K_{distr} as a function of pH at different chloride concentrations

K_{distr} is 379 at pH 7.8, and 856 in nitrate medium at pH 6.95. Chloride ions suppress yttrium (III) cations recovery to froth and shift pH of maximum recovery to the region of high values from 6.95 in nitrate medium to 7.8 at NaCl concentration of 0.01 M. When increasing sodium chloride concentration up to 0.05 M, yttrium (III) cations recovery to froth increases significantly. In the range of pH 4.0–9.0 the K_{distr} does not exceed 10. pH of maximum recovery at chlorides concentration of 0.05 M shifted insignificantly to the region of high values from 6.9 in nitrate medium up to 7.0.

Ytterbium (III) cations recovery at NaCl concentration of 0.01 M starts at pH 5.9 and reaches the highest value of 48 at pH 7.4. Maximum K_{distr} at chloride ions concentration of 0.05 M is 12 at pH 6.7. In the range of pH values from 4 to 6 and from 7.5 to 9 recovery is near zero.

RESULTS

In Table 1 the results of yttrium and ytterbium cations distribution coefficients calculations between froth pulp and chamber residue, onset and maximum recovery pH value, complexing and hydrating pH are shown.

Yttrium recovery in the absence of chloride ions at maximum recovery pH of 6.9 occurs in a form of $Y(OH)(DS)_2$, and at chloride concentrations of 0.01 M in a form of $Y(OH)_3$, because pH_{hydr} and pH_{compl} are 7.2 and 6.3 respectively [Kresh-

kov 1976]. At maximum recovery pH of 7.0 at chloride ions concentration of 0.05 M $Y(OH)_2 DS$ goes into the froth, because $pH_{compl} Me(OH)_2^+$ is 7.0, and pH_{hydr} is 7.2 [Gol'man 1982].

Ytterbium (III) hydroxo dodecyl sulfates $YbOH(DS)_2$ go into the froth up to $pH_{compl} Me(OH)_2^+$ 6.3, ytterbium (III) digidroxo dodecyl sulfates $Yb(OH)_2 DS$ in the range of pH from $pH_{compl} Me(OH)_2^+$ 6.3 to pH_{hydr} 6.6 and ytterbium (III) hydroxides at $pH > pH_{hydr}$ 6.6 [Chirkst et al. 2009c]. In the range of maximum recovery

Table 1. Rare-earth metals distribution coefficients as a function of recovery pH and sodium chloride concentration

Parameter	Y(III)	Yb(III)
$pH_{compl} MeOH^{2+}$	6.3	5.8
$pH_{compl} Me(OH)_2^+$	7.0	6.3
pH_{hydr}	7.2	6.6
$C_{NaCl} = 0$		
Distribution coefficient	855.6	403.7
pH of maximal recovery	6.9	8.3
pH of the start of recovery	6.1	6.0
$C_{NaCl} = 0.01 M$		
Distribution coefficient	379.5	48.3
pH of maximal recovery	7.8	7.4
pH of the start of recovery	6.7	5.9
$C_{NaCl} = 0.05 M$		
Distribution coefficient	9.4	12.4
pH of maximal recovery	7.0	6.7
pH of the start of recovery	6.4	6.0

Table 2. Yttrium and ytterbium chloro and hydroxo complexes instability constants

Compound	K_n	$\Delta_{compl}G_{298}^0$, kJ/mol	Compound	K_n	$\Delta_{compl}G_{298}^0$, kJ/mol
YCl ²⁺	0.054	-7.22	Y(OH) ²⁺	1.56×10 ⁻⁸	-44.56
YbCl ²⁺	0.110	-5.46	Yb(OH) ²⁺	4.99×10 ⁻⁹	-47.39

pH of 6.7 ytterbium (III) goes into the froth in the form of Yb(OH)₃, because pH_{hydr} is 6.6. pH of recovery onset 6.0 lies in the range of pH_{compl} MeOH²⁺ 5.8 and pH_{compl} Me(OH)₂⁺ 6.3 [Chirkst et al. 2010], therefore, Yb³⁺ is recovered in a form of YbOH (DS)₂.

The influence of chloride ions on the distribution coefficient was explained by comparing chloro and hydroxo complexes instability constants (Table 2). The first ones were calculated using the following formula:

$$\Delta_f G_{298}^0 \{MeCl_{aq}^{2+}\} = \Delta_f G_{298}^0 \{Me_{aq}^{3+}\} + \Delta_f G_{298}^0 \{Cl_{aq}^{-}\} + R \cdot T \cdot \ln K_n \quad (4)$$

by evaluating instability constant from the following equation:

$$K_n = e^{-\frac{\Delta_{compl}G_{298}^0}{R \cdot T}} \quad (5)$$

Gibbs energy of chloro complexes and lanthanide cations formation in aqueous solution was accepted according to the database [Database TKB]. Hydroxo complexes instability constants were accepted according to data [Chirkst et al. 2009].

When adding chlorides, part of lanthanides binds into non-floating chloro complexes. Decrease in hydroxo complexes part leads to flotation suppression and maximum recovery value shifting to higher pH values range. As a result, conditions for yttrium and ytterbium separation are provided.

Yttrium (III) cations are bonded into strong non-floating chloro complex, therefore, a significant decrease of distribution coefficients is observed. Because of comparatively high value of ytterbium (III) chloro complex instability constant, a decrease of recovery onset pH value and maximum recovery pH value when increasing chlorides concentration is observed.

Because of chloro and hydroxo complexes different stability, different shift of recovery pH and flotation suppression occur, and, therefore, the conditions for yttrium and ytterbium separation appear. The stronger the chloro complex and weaker the hydroxo complex are, the greater shift towards higher recovery pH values is.

CONCLUSIONS

1. During ytterbium ion flotation when adding chloride ions a tendency to K_{distr} decreasing and shifting maximum recovery to the region of lower pH values is observed. Yttrium K_{distr} also decreases, and maximum recovery pH at chloride concentration of 0.01 M shifts to the region of high values, compared to nitrate medium.
2. At maximum recovery pH yttrium goes into the froth at chloride concentration of 0.01 M in a form of Y(OH)₃, and at chloride ions concentration of 0.05 M the Y(OH)₂ DS goes into froth. Ytterbium (III) hydroxides are recovered into the froth at maximum recovery pH at NaCl concentration of 0.01 M, because pH_{hydr} 6.6 [8]. In the maximum recovery pH range of 6.7 with sodium chloride concentration of 0.5 M ytterbium (III) goes into the froth in a form of Yb(OH)₃.

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