

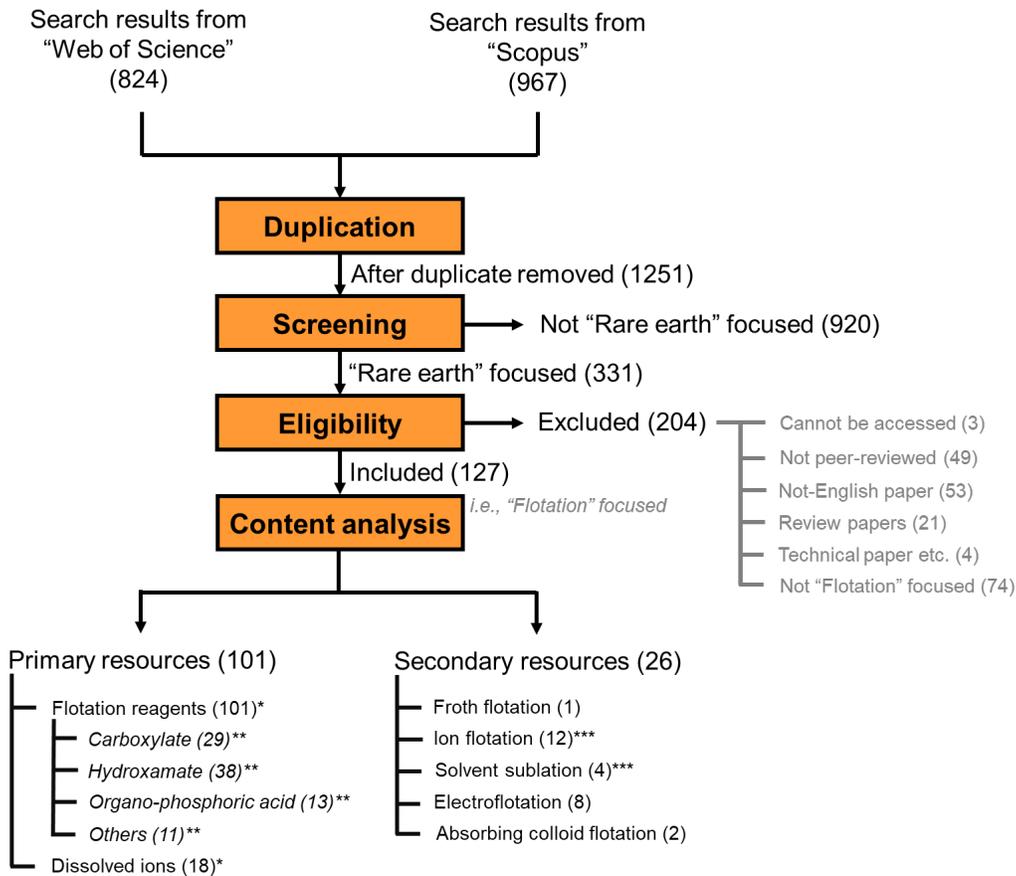
Supplementary Materials 1

Table S1. Lists of 17 REEs and 84 REMs used as searching keywords.

| Type of keywords | Keywords | References |
|----------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| Rare earth elements (REEs) | "Scandium", "Yttrium", "Lanthanum", "Cerium", "Praseodymium", "Neodymium", "Promethium", "Samarium", "Europium", "Gadolinium", "Terbium", "Dysprosium", "Holmium", "Erbium", "Thulium", "Ytterbium", and "Lutetium" | [3] |
| Rare earth minerals (REMs) | "Aeschynite", "Allanite", "Anatase", "Ancyrite", "Apatite", "Astrophyllite", "Baddeleyite", "Bariopyrochlore", "Bastnäsite", "Brannerite", "Britholite", "Brockite", "Burbankite", "Carbocernaite", "Caysichite", "Cerianite", "Ceriopyrochlore", "Cerite", "Chevkinite", "Churchite", "Cellophane", "Columbite", "Cordylite", "Crandallite", "Daqingshanite", "Davidite", "Eudialyte", "Euxenite", "Fergusonite", "Fersmite", "Florencite", "Fluocerite", "Fluorapatite", "Fluorite", "Formanite", "Gadolinite", "Gagarinite", "Gittinsite", "Gorceixite", "Goyazite", "Hellandite", "Hingganite", "Huanghoite", "Hydroxlapatite", "Iimoriite", "Joaquinite", "Kainosite", "Kamphaugite", "Karnasurtite", "Keiviite", "Kuliokite", "Lavenite", "Lessingite", "Leucophanite", "Loparite", "Lovchorrite", "Lueshite", "Miserite", "Monazite", "Mosandrite", "Parasite", "Perovskite", "Plumbopyrochlore", "Polycrase", "Polyolithionite", "Pyrochlore", "Rhabdophane", "Rinkite", "Rosenbuschite", "Sahamalite", "Samarskite", "Steenstrupine", "Stillwellite", "Synchysite", "Tengerite", "Thalinite", "Thorite", "Titanite", "Vesuvianite", "Wöhlerite", "Xenotime", "Yttrialite", "Yttrotantalite", and "Zirkelite" | [29] |

Table S2. Summary of recent studies on REM flotation using other collectors.

| Collectors | Samples | pH | Depressants | Recovery [%] | Grade [%] | References |
|--------------------------------------------------------|------------------------------------------------------|-----------|--------------------|---------------------|------------------|-------------------|
| Kerosene; mixed with fatty acid | Bastnaesite | 6 | – | 60–61 | – | [116,117] |
| Octanohydroxamic acid; mixed with sodium oleate | Bastnaesite | 7 | – | 94 | – | [118] |
| [N2222] EHEHP | Bastnaesite, fluorite, and calcite | 8–9 | Citric acid | 97 | – | [119] |
| [N4444] DEHP | Bastnaesite, quartz, and hematite | 5 | – | 90 | – | [120] |
| | Bastnaesite, monazite, calcite, dolomite, and quartz | 9 | – | 65–75 | 69.5 | [95] |
| Sodium dodecyl sulphate | Monazite, quartz, and hematite | 9 | – | 98 | – | [50] |
| Flotigam EDA | Allanite | 7 | Sodium silicate | 81 | 0.6 | [121] |
| R845N | Allanite | 5 | – | 64 | 1.0 | [121] |
| Fuel oil | Alaskan coal samples | 7 | – | 75–77 | 0.03–0.05 | [122] |



*, **, and *** some papers are belonged to more than one category.

Figure S1. Study selection flow diagram.

Figure S1 shows the flow diagram of the study selection in this review paper. The literature was systematically reviewed to answer this question using the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) guidelines to identify peer-reviewed journal publications that reported on “flotation” together with other keywords including “rare earth”, name of 17 rare earth elements, and name of 84 rare earth minerals as shown in Table S1. Web of Science and Scopus were selected as databases for this systematic review, and the publication dates were limited to between 2012 and 2021. The total search results are 1791 papers (from the Web of Science 824 papers and Scopus 967 papers) and after removing duplicate papers, the remaining numbers are 1251 papers. In the screening step, titles, highlights, abstracts, and keywords were checked to remove those that did not focus on “rare earth”. The 920 papers were removed, and the other 331 papers were moved to the next step. For the eligibility process, full-text articles were checked. The results showed that 3 papers cannot be accessed, 49 papers are not peer-reviewed, 53 papers are not written in English, 21 papers are review papers, 4 papers are technical papers, feature, focus, letters, and case studies, and 74 papers are not related to flotation. After the systematic selection, 127 papers remained and were used in this review. The selected papers are categorized into 2 main sections based on the contents; 101 papers go to section 3 “Rare earth flotation for primary resources” and 26 papers go to section 4 “rare earth flotation for secondary resources”.

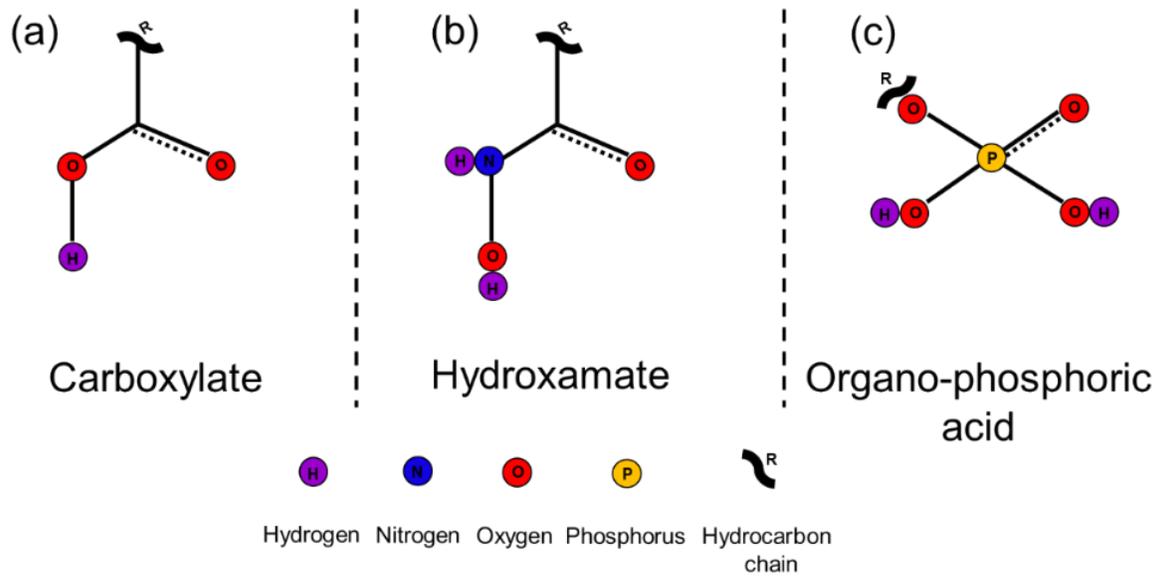


Figure S2. Chemical structure of typical three type collectors mostly used in REMs flotation carboxylate, (b) hydroxamate, and (c) organo-phosphoric acid. (a)

Figure S2 shows the chemical structure of all three types of collectors that are most frequently used in REMs flotation. Figure S2 (a) illustrates a chemical structure of carboxylate type collectors which the (RCOO^-) or $(\text{RCOO})_2^{2-}$ anion will form with rare earth ion be a $\text{RE}(\text{OOCR})_n$ at the REMs surface and rendering the REMs hydrophobic. Figure S2 (b) illustrates hydroxamate collector which usually has high potential to form complex with metal ion. It differs from carboxylate by a nitrogen atom which does not participate directly in bonding with a metal atom, but has an effect on the electron density on the O donor attached to it. The O donors in hydroxamate are weaker donors than carboxylate. It indicated that hydroxamate collectors prefer to form hydroxamate complex with rare metal ion than alkaline earth metals. Figure S2 (c) shows the typical chemical structure of organo-phosphoric acid type collectors. The $(\text{ROPO}_3\text{H}^-)$ and (ROPO_3^{2-}) are the dominant species that usually interact with rare earth ions on REMs surface [31–33, 106].

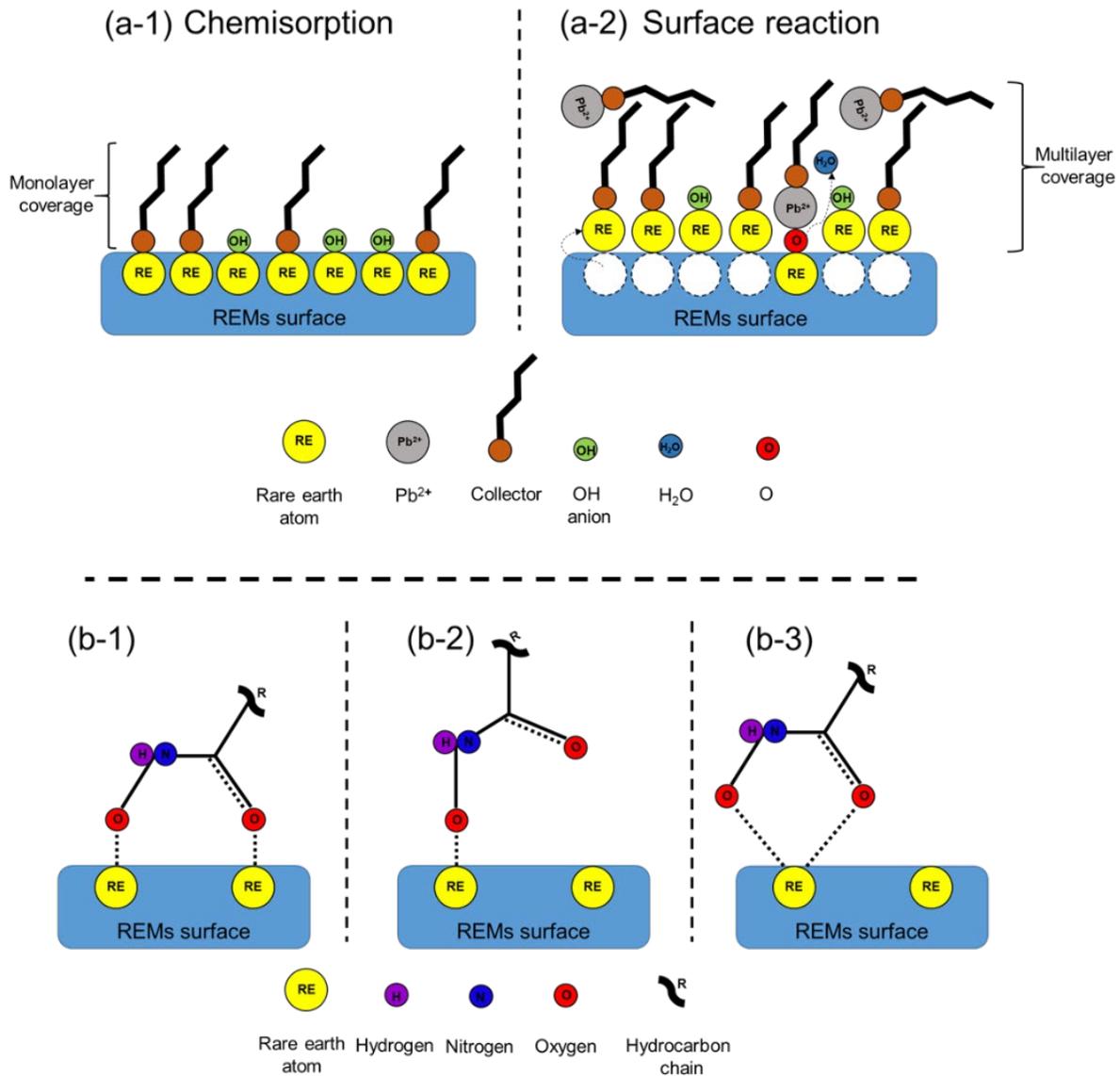


Figure S3. (a) Adsorption mechanism of collector on REM surface; (a-1) chemisorption and (a-2) surface reaction, and (b) chemisorption modes; (b-1) bridge, (b-2) monodentate, and (b-3) bidentate.

Figure S3 shows the adsorption mechanism of collectors on REMs surface. Chemisorption was shown in Figure S3 (a-1). The interaction of collectors and mineral surface occurred via covalence bonding of collectors and rare earth atom on surface of REMs without the movement of surface atoms. This adsorption mechanism was identified as 3 typical adsorption modes (i.e., bridge (Figure S3 (b-1)), monodentate (Figure S3 (b-2)), and bidentate (Figure S3 (b-3))). In addition, the adsorption layer of collectors most likely be a monolayer coverage. Another adsorption mechanism is surface reaction (Figure S3 (a-2)), this adsorption involves hydrolysis of metal atoms and formation of hydroxyl-complexes in solution then it will precipitated/re-adsorb on REMs surface that might be observe as a multilayer coverage [31,32,63–66,101].