Application Status of Rubidium, Cesium and Research Situation of its Separation from Brine with Solvent Extraction

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Abstract. Rubidium, cesium and its compounds play an important role in traditional and high-tech fields. This paper focuses on the research status of separation rubidium and cesium in brine using solvent extraction, and briefly introduced the characteristics of this method, which can be used to realize industrial production of rubidium and cesium from brine.

1. Introduction
A large number of natural salt lakes containing abundant rubidium and cesium resources in China, and its reserves are among the highest in the world [1]. Especially, separating rubidium and cesium from saline lake brines or underground brines has the value of development and utilization in Qinghai, Tibet, Xinjiang, Inner Mongolia and other regions, caused widespread highlight in the scientific community. Moreover, we has established the world's first Application Research Institute of Rubidium where specializing in the development and production of rubidium products [2]. Rubidium and cesium resources mainly exists in solid mineral and natural brine but separating from solid ore is a complex process with high cost, high consumption [3, 4]. However, there are 92% rubidium resources exists in saline lakes all over the world. Furthermore, rubidium and cesium are ions in brines where the separation process is relatively simple, low cost, less energy consumption. Therefore, it is the best material for separation and extraction of rubidium and cesium [4].

At present, the main methods for separation of rubidium and cesium are precipitation, ion exchange and solvent extraction methods. The precipitation method through the heteropolyacids reacting with rubidium and cesium generate precipitation to achieve separation, but the process is complex, low product purity, high production cost [5, 6]. The ion exchange method mainly used zeolite [7, 8], ferricyanide [9] and ammonium phosphomolybdate etc [10], but the low exchange capacity, the difficult adsorbent forming, the low mechanical strength, which seriously restricts its large-scale application and development. The solvent extraction method [11] can separate and enrich rubidium and cesium resources in saline lake brine containing low concentration of rubidium and cesium that has attracted great attention because high reaction speed, large processing capacity and continuous operation. Furthermore, the researches show that the solvent extraction method applied to separate rubidium and cesium from saline lakes and industrial intermediate liquids [1]. One of the most important is that the method has the industrial application prospect comparing with other methods. In
this paper, the separation of rubidium and cesium with solvent extraction are reviewed at home and abroad in recent years.

2. Application status of rubidium, cesium and its compounds
Rubidium (Rb) and cesium (Cs) are most active metal elements exist in all kinds of brines and easy to lose the outer layer electron [12]. The production and application of them are mainly concentrated in the USA, Japan, Russia, Europe and other developed regions in the world [13], where 80% used in high-tech fields, such as MHD power generation, ion propulsion engine, thermionic power conversion, cesium ion cloud communication and etc. There are 20% applied to traditional fields. For examples, biochemistry, electronics, catalysis, special glass, medicine and so on [13, 14]. Application of rubidium, cesium and its compounds for high-tech fields was widen with the birth of X-ray digital image intensifier, single crystal detector of cesium iodide and other high-tech products. From a worldwide perspective, rare metals rubidium and cesium are playing increasingly important roles in the fields of new energy, aerospace, national defense industry and other high-tech fields.

3. Research situation of separation rubidium and cesium in brine using solvent extraction
Solvent extraction utilizes the substance with different solubility or partition coefficient in two mutually insoluble solvents to realize separation and enrichment purposes. In recent decades, the separation of rubidium and cesium using solvent extraction are very active. Throughout the research situation at home and abroad, phenolic extractants and crown ether reagents have a better extraction effect for rubidium and cesium [15].

3.1. Phenolic extractants
Phenolic extractants, 4-Sec-butyl-2-(α-methylbenzyl) phenol (BAMBP) is an ideal extractant for rubidium and cesium. The extraction selectivity is Cs⁺ > Rb⁺ > K⁺ > Na⁺ > Li⁺. However, BAMBP is not suitable to industrial production due to low yield and expensive price. Nevertheless, 4-Tert-butyl-2-(α-methylbenzyl) phenol (t-BAMBP) is an isomer mutual with BAMBP that can avoid the former deficiencies, which becomes the hotspot of industrial application and research [12]. The structure of t-BAMBP is shown in Figure 1 [11].

![Fig 1. t-BAMBP](image)

The reaction principle of extraction Rb⁺ and Cs⁺ from brine with t-BAMBP: The H⁺ dissociate from phenolic hydroxyl and exchange with Rb⁺ and Cs⁺ in the aqueous on alkaline condition then formation its hydrophobic phenolic acid salts into organic phase. Finally, it can be stripped by strong inorganic acid so that realize the separation and extraction of Rb⁺ and Cs⁺ from brine [16].

In recent decades, solvent extraction has been widely investigated with the advantages of large handling capacity, simple equipment, rapid reaction, simple process, low cost, easy to achieve the continuous operation and etc [4, 17]. The extractant t-BAMBP are widely used in extraction due to less toxicity, small water-soluble, strong selectivity and easy stripping [18]. The influences of aqueous
alkalinity and concentration, organic-aqueous phase ratio, extraction time and temperature, type of thinner were investigated by J.Y. Yang [16] and Z.Y Chen [18], the results provided a reasonable process parameters for the extraction of \( \text{Rb}^+ \) and \( \text{Cs}^+ \) from brine by 5-stage countercurrent extraction with 1.0 mol/L t-BAMBPs in xylene, the initial concentration of \( \text{K}^+ \) and \( \text{Rb}^+ \) respectively as 0.116 mol/L and 0.091 mol/L, 1.0 mol/L aqueous alkalinity, organic-aqueous phase ratio \( (O/A=20/6) \), extraction time 3 min, extraction temperature 298 K. Z. Lu [19] researched the extraction of rubidium and cesium from brine containing high potassium using t-BAMBP with xylene as diluent that the purity of \( \text{RbCl} \) products reached 99.80\%, the extraction rate was 97.00\%, the stripping rate of rubidium was 98.40\%, the final extraction yield of \( \text{Rb}^+ \) reached 95.55\% with 1.0 mol/L initial t-BAMBP concentration in xylene, 1.0 mol/L aqueous alkalinity, organic-aqueous phase ratio \( (O/A=3/1) \), extraction time 2 min. L.Y. Hu [20] researched the extraction of rubidium and cesium using t-BAMBP from the liquor after extracted lithium and potassium of lapidolite in Yichun, Jiangxi (China), total metal recycling rate of \( \text{Rb}>94.00\% \), \( \text{Cs}>98.00\% \) and the products quality more than the industrial grade product of KBI company in the USA. Furthermore, the author also carried out the experiments using t-BAMBP extraction of rubidium and cesium in brine from somewhere containing high potassium, calcium and magnesium ions, but the results is not ideal with ultra-high potassium content in the brine. Moreover, the brine containing high concentration calcium and magnesium ions cannot be directly extracted using t-BAMBP owing to the excessive alkali consumptions, demanding equipment’s, and may be these limits it applies to the industrial production.

3.2. Crown ether reagents

Crown ether, a coronal compound with hole structure, mainly reacts complexation reaction with cations and alkali metal ions. The complexation selectivity depends on the size of the cavity and the type of substituent [21], when the hole size is similar to the alkali metal ions that formed the most stable complex with high selectivity. For example: 18-crown-6 (Figure. 2, aperture 0.26 ~ 0.32 nm) is similar to \( \text{Rb}^+ \) (diameter 0.3294 nm). Correspondingly, 21-crown-7 (aperture about 0.34 nm) and \( \text{Cs}^+ \) (diameter 0.334 nm) have the same size [22].

![Figure 2. 18-Crown-6](image)

C. Alfieri et al [23], who opened the prelude for the extraction of alkali metals by crown compounds, firstly synthesized and characterized crown compounds 1, 3 alternate-p-tert-butyl Alix crown 6 that has the ability to recognize metal ions due to its cavity contains atoms O, N or S. B.S. Mohite et al [24] proved the extraction rate of rubidium decrease with the increase of potassium concentration and is up to 100\% with 18 crown 6 (DC18C6) as extractant, dichloroethane as diluent and \( \text{pH}=3 \sim 7 \). M.M. Liu [25] researched the extraction of cesium in geothermal water using “dibenzo-21-crown 7 and ionic liquid as extraction system” at the first time. The results show that single stage extraction rate of cesium was above 75\%, but it is worth noting that the stripping of cesium is difficult. Furthermore, he puts forward to recycle rubidium and cesium elemental or alloy with non-aqueous electrochemical, so as to avoid the destruction of the ecological environment in the extraction process using traditional organic solvent, but the related work has yet to be explored systematically. At last but not least, the crown ethers and their derivatives were used to separate \(^{137}\text{Cs} \) in high level radioactive
waste [26] in general, there are no related industrial applications reported because of the difficulty in synthesizing and the high price.

4. Conclusion
Rubidium and cesium resources are rich in saline lakes and its application research achieved corresponding achievement in high-tech fields. Solvent extraction method for the separation and extraction of brine with low concentration rubidium and cesium achieves the corresponding laboratory research results, but the industrial production has not been reported yet up to now. The method using t-BAMBP shows the superiority compared with other methods. However, the results are not ideal with the brine containing high potassium. Besides, higher alkali consumptions, higher requirements on equipments, all these factors limit its industrial application. In view of these difficulties, the related researches need to be unfolded systematically.

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