

Natural Resources and Environmental Issues

Volume 15 *Saline Lakes Around the World:
Unique Systems with Unique Values*

Article 42

2009

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Recommended Citation

Dong, Ya Ping; Meng, Qing Fen; Feng, Hai Tao; Cui, Xiang Mei; Xu, Bin; Wu, Wei; Gao, Dan Dan; and Li, Wu (2009) "Separation and economic recovery of strontium from Nanyishan oil-field water, China," *Natural Resources and Environmental Issues*: Vol. 15 , Article 42.

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Separation and economic recovery of strontium from Nanyishan oil-field water, China

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Separation and Economic Recovery of Strontium from Nanyishan Oil-field Water, China

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ABSTRACT

The mass ratio of Ca to Sr is greater than 10 in Nanyishan oil-field water, which causes significant problems during the economic extraction and recovery of selected trace elements in the oil-field water. The oilfield water was isothermally evaporated and various salts such as Li, K, Mg, Ca, Na, Sr, Rb, Cs, Br, and I were obtained from the solution. The Sr content of each phase was determined by ICP-AES, the Sr distribution rule in this process was obtained, and the best separation stage for Sr was identified, to optimize the separation of Sr from Nanyishan oil-field water.

INTRODUCTION

With a content of 0.02-0.04% in the crust and 0.048% on the Earth's surface, Sr is the least abundant of all alkaline earth metal elements. It rarely appears as a high-grade ore body because of its geochemical nature. The most commonly occurring Sr minerals are celestite (SrSO₄) and strontianite (SrCO₃). Presently the Sr-producing industry mainly processes solid Sr ore. Presently most of the world's Sr is produced from mining and processing Sr ore; however, oil-field brines and other naturally occurring aqueous solutions may present a more economical Sr source. Many reports exist on Sr in aqueous solution. We present the first documentation of Sr production from a brine system rich in Ca.

Sr, Ca, Mg and Ba are all alkaline earth metal elements. Because of their high chemical activity they can only exist in the form of compounds in nature and not in their elemental state. This high chemical activity makes it very difficult to separate these alkaline earth elements, particularly the separation of Sr from Ca. Separation methods currently in use include extraction, ion exchange chromatography, and liquid membrane separation.

Among the most effective and widely used extraction agents are crown ethers such as dicyclohexyl-18-crown-6 (DCH18C6)-octanol (He et al. 1995; Ju 2002), 15-crown-5

(B15C5) (Vanura & Makrlík 2002; Vanura et al. 2002) and others. Although crown ethers are superior extractants for Cs(I), they are too expensive and need to be diluted by halogenated hydrocarbons, which upon irradiation produce hydrochloric acid, which can corrode equipment. This restricts their application in industrial operations.

The ion exchange technique focuses on a separation system for the decontamination of radioactive waste containing low Sr content (Chadfield 1998). According to the separation mechanism, liquid chromatography can be divided into liquid-liquid distribution chromatography, liquid-solid adsorption chromatography, and others. Some widely used liquid stationary phases are 1,2-bis-(2-cyanoethoxy)propane (ODPN), polyethylene glycol (PEG) (Herbst & Law 2002a, 2002b), octadecylsilyl (ODS), squalane, and bis-2-ethylhexylphosphinic acid. Wang & Nagaosa (2003) separated Ca, Sr, Mg and Ba from aqueous solutions within the pH region of 5.3-6.5 units by using bis-2-ethylhexylphosphinic acid as the stationary liquid, 0.1 mol l⁻¹ chloroacetic acid containing 5% ethyl alcohol as the mobile phase, and this enabled effective separation of these four alkaline earth metal elements.

The liquid membrane technique is a separation operation with a membrane as the separation medium and the concentration gradient as the driving force. A liquid membrane is a very thin layer of emulsion particles suspended in liquid, which can separate two mutually soluble solutions due to the infiltration phenomenon. Based on their structure, such membranes can be divided into many types, of which three have found practical application: the emulsion membrane, the supported liquid membrane (Lee & Hong 2000) and the fluid membrane (Shamsipur & Raoufi 2002). Wang & Li (1997) studied a liquid membrane for the separation and enrichment of Sr. The system included a coordination flowing carrier (PMBP TBP), a surfactant (SPAN 80), an intensifier (glycerol), a solvent (hexylene) and an internal phase (1.2 mol l⁻¹ hydrochloric acid). The efficiency of Sr enrichment proved to be above 99.5% under external phase (pH = 7-8).

Table 1—Composition (in weight percent) of the brine raw material.

Ion	Li ⁺	Na ⁺	K ⁺	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	Sr ²⁺	B ₂ O ₃	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	I ⁻
%	0.021	7.83	0.78	0.092	1.43	0.082	0.13	0.27	15.73	0.022	0.011	0.0031

Table 2—Test results of the evaporation concentration process of oil-field brine.

Sequence number	Density (g/ml)	Initial material mass (kg)	End material mass (kg)	Solid mass (kg)	Liquid mass (kg)	Rate of salt crystallization (%)	Comments
0	1.2019	56.50	56.50	0.00	56.50	0.00	Initial material
1	1.2560	56.50	27.50	9.90	17.60	17.52	NaCl
2	1.2890	17.60	13.64	1.38	12.26	2.44	NaCl
3	1.3375	12.26	9.54	1.12	8.42	1.98	Sylvite
4	1.3856	8.42	7.04	0.64	6.40	1.13	Carnallite complex salt
5	1.4239	6.40	5.29	0.79	4.48	1.40	Precipitated Antarcticacite
6	—	4.48	4.48	0.22	4.26	0.39	Antarcticacite
7	1.4431	4.26	4.26	0.86	3.40	1.52	Antarcticacite

Rich in Sr resources, China has the largest Sr reserves and is the biggest Sr supplier of the world, supplying two thirds of the global market. Due to the many years of exploitation of solid Sr mines (chiefly in the form of celestite), domestic exploitation of mines has now reached the final stage. Fortunately, there are abundant underground brine resources in the Qaidam basin. Their contents of K, Ca, Li, B, Br, I, Sr, Rb and Cs are large, with especially large concentrations in the oil-field water (Lu 1978; Li et al. 2001). Thus, these brines have great potential for large-scale industrial exploitation. Brine utilization can relieve the condition of insufficiency of the relevant resources. The exploitation of oil-field water resources can also actively impact the national economy, as well as aid the development of the local economy of Qinghai. Sr concentration is high in the oil-field water. For example, in the Nanyishan oil-field brine of Qaidam basin the average Sr concentration reaches 5364 mg I⁻¹, which generally exceeds the minimum concentration for industrial exploitation (Qinghai Geological Survey Institute 2003). The Nanyishan oil-field brine can be classified as a calcium chloride type brine. To rationally utilize these local resources, their existence and transformation characteristics need to be studied.

MATERIALS AND METHODS

The raw material for the experiment is the highly saline brine present in the third stratum of the west Qaidam basin. The brine was roughly divided into the Nanyishan K, B, Li, I bonanza area and the prospective enrichment area of Xiaoliangshan, Youquanzi, Kaitemilike, and Youdunzi. The Nanyishan tectofacies is located in a grade-3 tectonic belt in the west Qaidam basin discovered during a geological survey in 1955. The Nanyishan oil-water lake lies in the center of the tectofacies in a low-lying alluvial landscape. The latitude of the lake is 37°50'-38°35' north, and the longitude is 91°07'-92°10' east. It is a surface water field that spreads NW-SE, from the Sheng 202 well in the east to the Qian 8-1 well in the west. The oil-field water was released to the surface by an out of control oil-gas well. The area of the lake is 0.5 km² with a maximum depth of 1.75 m and an average depth of 0.97 m. The lake water is greenish blue, smells of oil and is greasy to the touch. Chemical analysis of water samples indicates that the concentration of Cl⁻ is much higher than that of Na⁺. The oil-field water should therefore be classified as a CaCl₂ type in Sulin's classification (Zhang 1979), characterized by high Ca²⁺, high Cl⁻ and low SO₄²⁻ and Mg²⁺ concentrations.

There is little vertical variation in ionic concentrations, and salinity variations from the edge to the center are slight. The shallower the lake water, the higher the salt concentration. The main elements of economic value are K, B, Li, I, Rb, Cs, and Sr, and they are homogeneously distributed (Duan & Yuan 1988; Fu et al. 2005; Xiong et al. 2005).

Using Nanyishan oil-field brine as raw material (composition listed in Table 1), an indoor evaporation experiment was performed in plastic evaporation containers using an IR lamp and an electric fan. The amount of water evaporated was calculated using a phase diagram of NaCl-KCl-MgCl₂ system. The distribution rules of each mineral and the extent of Sr enrichment were determined by analysis of the brine and the deposited solid minerals. In the process of the evaporation experiment, a densimeter was used to measure the solution density.

RESULTS AND DISCUSSION

The crystallization of salts during the evaporation concentration process of oil-field brine, the process data, and the change in concentration of Ca and Sr during the different stages of the process are shown in Figure 1, Table 2, and Table 3, respectively. The oil-field brine evaporated at room temperature until NaCl precipitated first. After separation of the solid from the liquid, the liquid evaporated until KCl saturated, when NaCl and KCl precipitated. After separation, evaporation was continued with subsequent precipitation of B, NaCl and KCl. By controlling the evaporites, three minerals containing B, K, Na and Mg were separated from the liquid. The remaining liquid was enriched in the rare dispersive elements. Evaporation rates of the remaining liquid were reduced when compared with earlier stage evaporation rates.

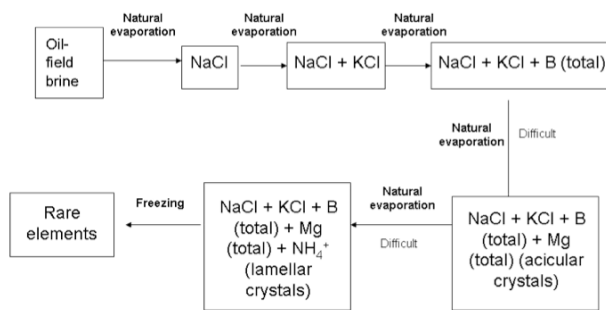


Figure 1—Salt crystallization during the evaporation condensation process of oil-field brine.

The oil-field brine contains different useful components. For the development of a comprehensive production process, the elucidation of the distribution laws of these compounds is essential. The evaporation experiment at room temperature provided useful information on the distribution of Sr in the oil-field brine. The precipitation process of the elements in oil-field brine follows the phase diagram law of the NaCl-KCl-MgCl₂-H₂O system in the initial phase of the evaporation condensation process. NaCl precipitated first, followed by precipitation of carnallite from the saturated brine. During further condensation of the liquid, the brine reached the co-saturation point of K-Mg, and a mass of acicular crystals precipitated from the solution (Cui et al. 2008).

Table 3—The concentration variation of Ca and Sr during the evaporation condensation process.

Density (g/ml)	Liquid Ca (%)	Liquid Sr (%)	Solid Ca (%)	Solid Sr (%)
1.2019	1.43	0.129	—	—
1.2560	4.46	0.400	0.32	0.034
1.2890	6.16	0.577	0.56	0.024
1.3375	8.88	0.827	1.04	0.099
1.3856	11.30	1.073	2.76	0.280
1.4239	12.93	1.256	6.31	4.070
—	—	—	14.69	4.360
1.4431	14.02	0.990	15.93	1.340

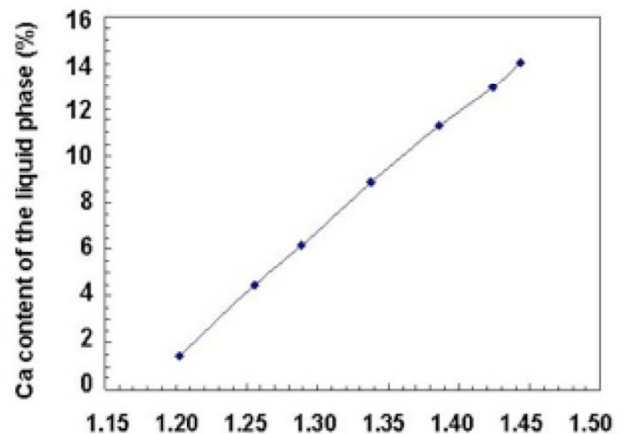


Figure 2—The enrichment trend of Ca in the liquid-phase during the room temperature evaporation condensation process.

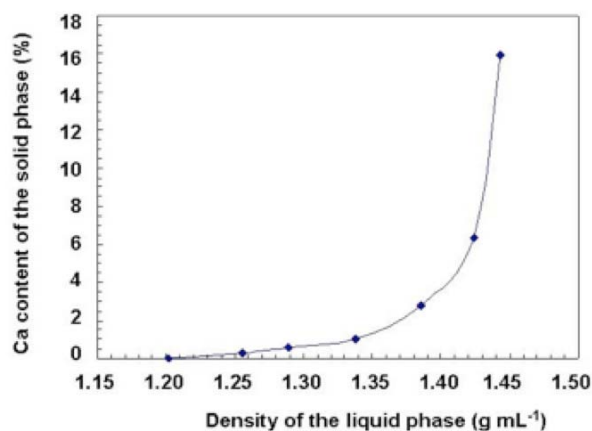


Figure 3–The enrichment trend of Ca in the solid-phase during the room temperature evaporation condensation process.

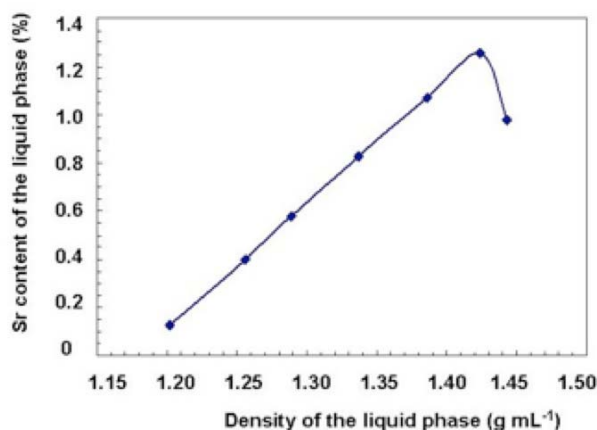


Figure 4–The enrichment trend of Sr in the liquid-phase during the room temperature evaporation condensation process.

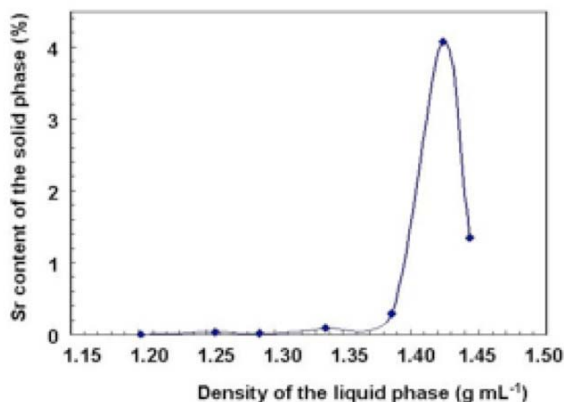


Figure 5–The enrichment trend of Sr in the solid-phase during the room temperature evaporation condensation process.

The density of the brine increased during the condensation process, the rate of change in density decreasing during mineral precipitation. After separation of the solids from the liquid, we studied the enrichment of Sr and of Ca in the solid and the liquid phase by separately analyzing the concentrations of these elements in the different phases (Figure 2–5).

The Sr content of each phase was determined by ICP-AES. The Ca content was analyzed by mass titration using EDTA standard solution as titrant. Analysis of the solids showed that Ca and Sr remained in the liquid phase, and that little was found in the solid-phase at the stage of NaCl and carnallite precipitation. During carnallite precipitation, Ca and Sr were further enriched in the liquid phase, and the concentration of these elements in the solid phase increased, mainly due to entrapment of mother solution. With the continuation of evaporation and condensation, the Ca and Sr contents in the solid-phase further increased while they approached saturation in the liquid. Compounds of Ca and Sr could then be obtained from the solid phase following further evaporation. The Ca content in the solid-phase increased in a linear fashion (Figure 2 and 3). When the density of the solution reached 1.4239 g mL⁻¹, the Ca content of the solid phase increased dramatically to a maximum of 15.93%. This shows that Ca precipitated instantly from the liquid phase, and that at the same time its concentration in the liquid phase kept increasing. The changes in Sr concentration in the liquid and the solid phase are shown in Figure 4 and 5, respectively. The Sr content of the liquid-phase increased with the density of the solution, and reached its maximum when the density reached 1.4239 g mL⁻¹. During further evaporation, the Sr content in the liquid phase began to decrease. Initially the Sr content in the solid phase increased at a low rate. When the brine density reached 1.4239 g mL⁻¹, Sr largely precipitated from the liquid phase, and its content in the solid phase reached more than 4%. This concentration is appropriate for Sr extraction. At the same time, massive amounts of Ca salts precipitated, and Ca and Sr were found in the solid phase at a ratio of 1.5:1, a value that increased further with the continuation of the process. To monitor the precipitation process in detail, we refined the brine evaporation experiment by adding Sr compounds and by increasing sampling times. When this stage was well controlled, we could obtain about 20% Sr compounds from oil brine that initially contained only about 0.037% Sr. Extraction of Sr did not affect recovery of potassium. A study of the relationship between the separation of Sr, Rb and Cs is

underway. Figure 6 shows the principal process that is to be adopted, based on our experimental results (Wu 2007).

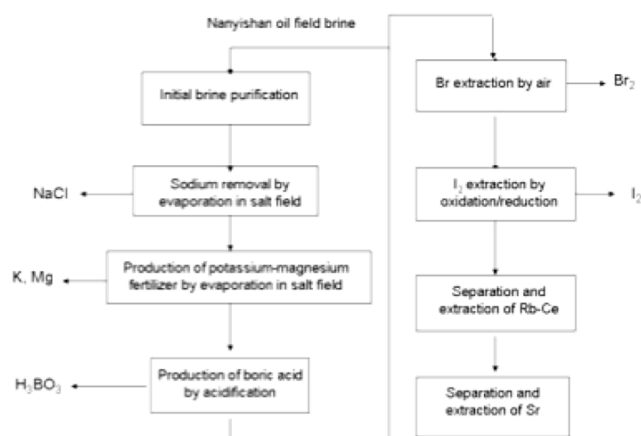


Figure 6—Schematic diagram showing the process of separation and extraction of strontium and other chemical elements from oil-field brine in Nanyishan.

CONCLUSIONS

Four conclusions can be drawn from the results of the Nanyishan oil-field brine evaporation experiment at room temperature:

1. Separation and extraction of valuable components from oil-field water is a complex process. Different interactions exist between the different components.
2. As oil-field brine mainly consists of Ca chloride, Ca must first be separated from Sr to enable the effective recovery of Sr.
3. Ca and Sr are concentrated in the liquid phase at the stage of potash precipitation due to evaporation. After many types of potassium salts have precipitated, Ca and Sr become saturated in the liquid phase. When evaporation continues and the liquid phase becomes further concentrated, Ca compounds co-precipitate with Sr salts.
4. Using different technological processes, Sr can be extracted either from the liquid or from the solid phase.

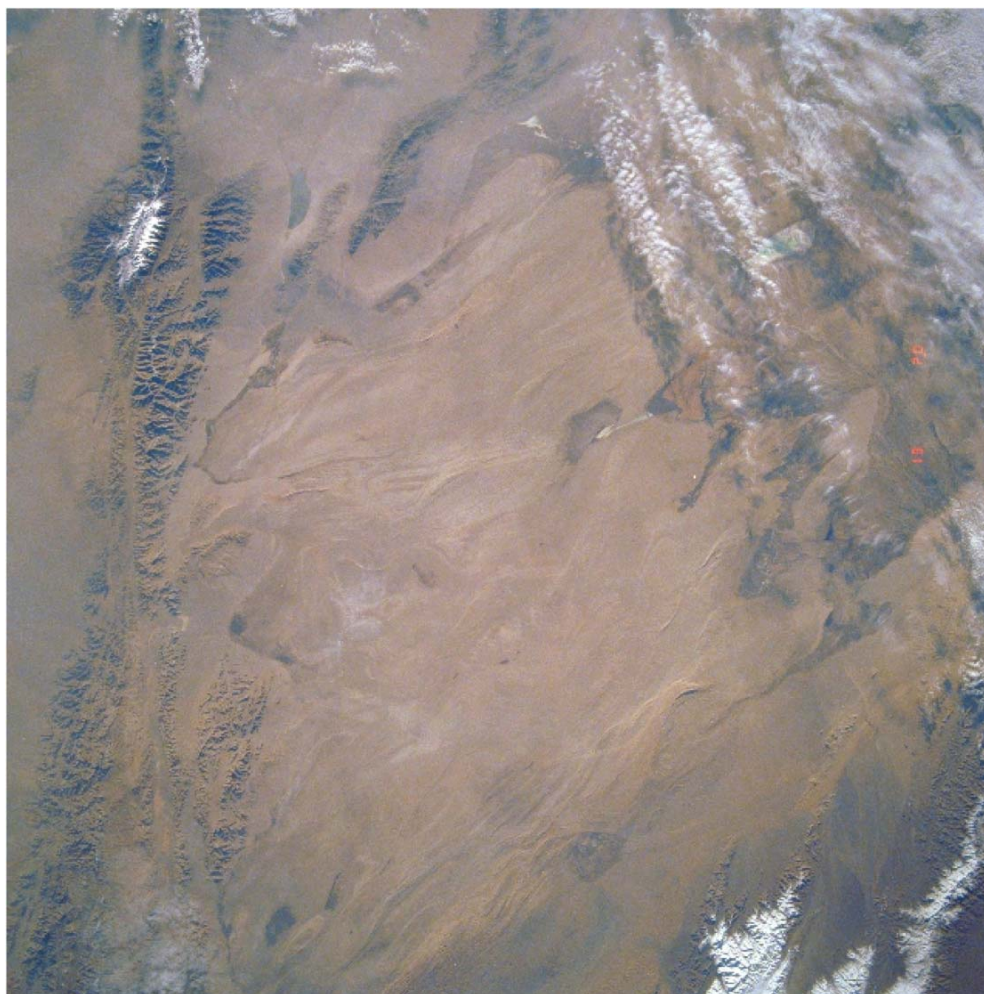
ACKNOWLEDGEMENTS

The authors appreciate the financial support of “The Eleventh Five-Year Scientific Support Plan” of the Ministry of Science and Technology of China, Qinghai Science and Technology Department, the western light personnel training plan of the Chinese Academy of Sciences and Qinghai Institute of Salt Lakes.

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