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Application of chemical equilibrium modeling in concentration process for strontium recovery from SWRO brine

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ABSTRACT

In this study, the simulation of concentration process was conducted by PHREEQC software for evaluation of strontium recovery in various concentration steps with gradient evaporation experiment by seawater reverse osmosis brine. The results of modeling were similar to experiment in majority of ions but strontium was a quite different. Magnesium, potassium and boron were concentrated up to 7 times and sodium and calcium were slightly different from them, it causes influence of co-precipitation on deposition of sodium chloride and concentration of chloride for counter ion which strontium and calcium. Therefore, the proper concentration factor for strontium recovery is 3 times such as pre-concentration.

Keywords: Strontium; Metal extraction; PHREEQC; Valuable resource recovery; Seawater desalination concentration; Seawater reverse osmosis brine

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1. Introduction

The seawater desalination method that uses the reverse osmosis membrane is widely used over the whole world recently. In this kind of the seawater desalination process, the part which becomes a problem that is the discharge of the concentrated water which is named brine or SWRO brine. The recovery rate of seawater reverse osmosis (SWRO) is determined according to the target quantity of treated water and concentrated water. General quantity of concentrated water at commercial SWRO plant is about 55% of feed which is seawater [1]. Moreover, the quality of concentrated water also depends on recovery rate but general salinity of concentrated water is about twice of the feedwater so the concentrated water from SWRO is appeared main problems in SWRO plant. There is possible of impact to marine environment when high concentrated water is entered. The balance of feedwater has impact in long term and ecosystem of seawater is able to have damage [2–4]. Recently, influence of the fishing activity and the cause of the followed ecological problem have been researched for marine ecosystem. Beside, disposal of concentrated water also has been researched that solar evaporation, to reduce quantity of brine by near zero liquid discharge, advanced oxidation process (e.g., ozonation, Fenton process, photocatalysis and photooxidation, sonolysis and electrochemical oxidation) and recovery of valuable resource [5].

Seawater is composed of various ions such as sodium, chloride, sulphate, potassium, calcium, magnesium, strontium and even lithium. Some particular ions which are sodium chloride, potassium chloride and magnesium chloride have been already produced for commercial production using seawater [4]. Furthermore, valuable ions which are cesium, rubidium, lithium, uranium, boron and strontium of recovery technology have been researched from seawater [6–10]. The technical approach of collecting the valuable ions from seawater is fundamental preparation for depletion of the resource, resource trade disputes, etc.

Strontium (Sr) is able to be one of the beneficial ions because of abundant ion in seawater. It is much dissolved (about 6–7 mg/L) among the cations in seawater, so it is useful for development [11]. Moreover, it is an almost twice concentration

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of average concentration in seawater so that is better environmental which is concentrated water in comparison with general extraction process from seawater. Recently, research of strontium recovery which is using titanate nanotube or alginate microsphere has been tried from seawater [9,10]. Strontium compounds are applied to many industrial such as fireworks, ferrite ceramic magnet and zinc production. The key factor is one of extraction of the valuable resource in seawater is concentration process. The majority of ions are low concentration and there is necessary for minimum concentration to produce the commercial production. As concentration processes proceed, chemicals are crystallized, which are quite complicated chemical mechanisms are involved. Therefore predicting concentration process, as followed crystallization is one of the important what we should know to design the extraction process.

Table 1
The ion concentration of SWRO brine

	Concentration (mg/L)
Li	0.35
Ca	822.8
Mg	2,438
Na	19,704
K	714
Si	3.03
B	8.36
Sr	14.4
Cl	34,087.3
SO_4	4,800.7
Br	125.4

In this study, we evaluate possibility for strontium recovery in various concentration factors and simulate the ion concentration by calculation program for optimum concentration factor.

2. Materials and methods

The concentration process was used to evaluate in comparison with calculated ion concentration with evaporation concentration. For the experiment of feedwater was prepared by SWRO desalination pilot plant of Gwangyang, South Jeolla Province, Korea. With average production of 100 m^3/d (which 50% of recovery of feed), it was only designed for research of desalination. Basic condition of SWRO brine as feed solution was generally 28,000–32,000 mg/L of total dissolve solid (TDS) and 7.8 of pH. To determine the pH and TDS of SWRO brine were used pH meter (Orion 5 star) and conductivity meter (JENWAY 4520). The composition of major ions of feed solution is shown in Table 1. Experiment was carried out by setting each 10 L of SWRO brine and conducted by evaporating concentration in gradual stages as 2, 3, 5 and 7 times. The samples of solution after work were filtered from 0.5 μm pore size membrane of polytetrafluoroethylene using a syringe and samples of sediment as by-product were dried at 100°C for 24 h. The ion concentrations of solution were analyzed by ion chromatography and inductively coupled plasma optical emission spectrometry (Ciros vision) at the end of each experiment. To check the solid phase of sediment generated from evaporating concentration was determined by X-ray diffractometer (Rigaku primus II) for analyzing composition of solid.

The prediction of ion composition and pH using PHREEQC was calculated by Pitzer activity coefficients which is Pitzer–Debye–Hückel term [12]. PHREEQC is the

Table 2
The potential compounds of SWRO brine (predicted by PHREEQC)

Compound	Formula	Compound	Formula	Compound	Formula
Anhydrite	$CaSO_4$	Halite	NaCl	Pirssonite	$Na_2Ca(CO_3)_2$:$2H_2O$
Aragonite	$CaCO_3$	Hexahydrite	$MgSO_4$:$6H_2O$	Polyhalite	$K_2MgCa_2(SO_4)_4$:$2H_2O$
Arcanite	K_2SO_4	$K_2B_4O_7$:$4H_2O$	$K_2B_4O_7$:$4H_2O$	Portlandite	$Ca(OH)_2$
Bischofite	$MgCl_2$:$6H_2O$	Kainite	$KMgClSO_4$:$3H_2O$	Quartz	SiO_2
Bloedite	$Na_2Mg(SO_4)_2$:$4H_2O$	Kalicinite	$KHCO_3$	Schoenite	$K_2Mg(SO_4)_2$:$6H_2O$
Borax	$Na_2(B_4O_5(OH)_4)$:$8H_2O$	KB_5O_8:$4H_2O$	KB_5O_8:$4H_2O$	SiO_2(a)	SiO_2
Boric_acid(s)	$B(OH)_3$	Kieserite	$MgSO_4$:H_2O	$Sr(OH)_2$(s)	$Sr(OH)_2$
Brucite	$Mg(OH)_2$	Labile_S	$Na_4Ca(SO_4)_3$:$2H_2O$	$Sr(OH)_2$:$8H_2O$(s)	$Sr(OH)_2$:$8H_2O$
Burkeite	$Na_6CO_3(SO_4)_2$	Leonhardite	$MgSO_4$:$4H_2O$	$SrCl_2$(s)	$SrCl_2$
Calcite	$CaCO_3$	Leonite	$K_2Mg(SO_4)_2$:$4H_2O$	$SrCl_2$:$2H_2O$(s)	$SrCl_2$:$2H_2O$
Carnallite	$KMgCl_3$:$6H_2O$	Magnesite	$MgCO_3$	$SrCl_2$:$6H_2O$(s)	$SrCl_2$:$6H_2O$
Celestite	$SrSO_4$	Mirabilite	Na_2SO_4:$10H_2O$	Strontianite	$SrCO_3$
Chalcedony	SiO_2	Misenite	$K_8H_6(SO_4)_7$	Sylvite	KCl
Dolomite	$CaMg(CO_3)_2$	NaB_5O_8:5H2O	NaB_5O_8:$5H_2O$	Syngenite	$K_2Ca(SO_4)_2$:H_2O
Epsomite	$MgSO_4$:$7H_2O$	$NaBO_2$:$4H_2O$	$NaBO_2$:$4H_2O$	Teepleite	$Na_2B(OH)_4Cl$
Gaylussite	$CaNa_2(CO_3)_2$:$5H_2O$	Nahcolite	$NaHCO_3$	Thenardite	Na_2SO_4
Glaserite	$NaK_3(SO_4)_2$	Natron	Na_2CO_3:$10H_2O$	Trona	$Na_3H(CO_3)_2$:$2H_2O$
Glauberite	$Na_2Ca(SO_4)_2$	Nesquehonite	$MgCO_3$:$3H_2O$		
Gypsum	$CaSO_4$:$2H_2O$	Pentahydrite	$MgSO_4$:$5H_2O$		

Table 3
Results of experiment and calculation

	SWRO brine	2 Times		3 Times		5 Times		7 Times	
	Experimental	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
Ca	823	1,500	1,480	910	1,248	565 ± 66	702	409 ± 25	443
Mg	2,438	5,194	5,086	8,479	7,672	12,443 ± 701	12,513	16,916 ± 1,071	177,21
Na	19,704	40,768	41,399	67,459	62,505	94,926 ± 2,268	102,460	100,421 ± 2,460	116,665
K	714	1,528	1,500	2,547	2,265	3,709 ± 412	3,713	5,017 ± 506	5,265
Li	0.35	0.67	0.74	1.02	1.11	1.52 ± 0.3	1.82	2.13 ± 0.5	2.58
Si	3.03	7.59	2.74	6.79	2.49	10.59 ± 0.59	1.98	12.00 ± 4.24	1.74
B	8.36	19.00	17.57	29.00	26.52	42.70 ± 5.23	43.47	57.25 ± 7.42	61.65
Sr	14.4	27.0	26.6	37.0	21.5	2.1 ± 0.45	10.4	4.3 ± 3.27	5.7
Cl	34,087	70,792	71,613	120,362	108,123	179,214 ± 11,577	177,239	185,467 ± 2,451	207,188
Br	125	209	263	364	397	515 ± 64	650	594 ± 235	922
SO_4	4,801	19,404	9,631	15,149	12,181	16,555 ± 290	16,589	21,429 ± 3,297	221,90

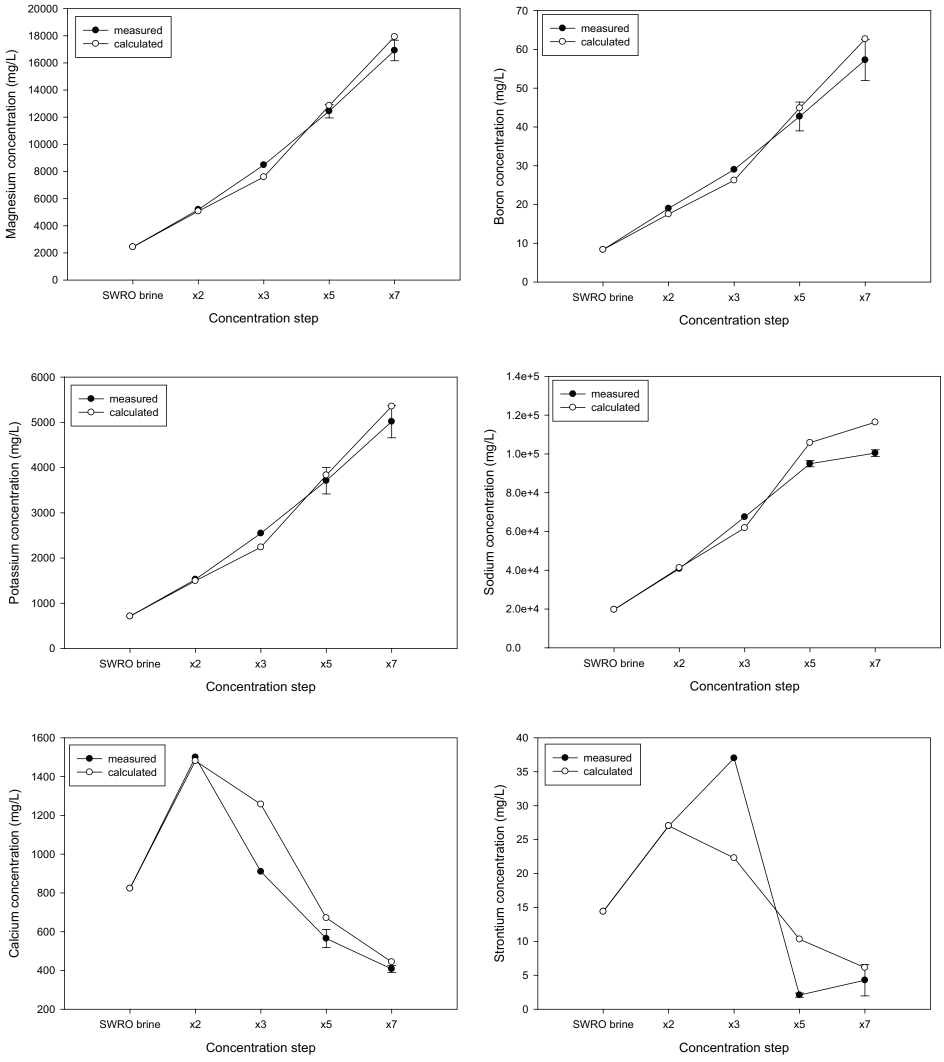

Fig. 1. The comparison result of experiment and calculation for extractable ion (Mg, B, K, Na, Ca and Sr).

software for equilibrium program, a geological solubility program which is able to be applied to the calculation of concentration by evaporation or injection of salts [13]. The Pitzer approach can be also applied to appropriate model for high concentrated solutions such as seawater, due to long and short range interactions in solute species [12–15]. In this study, to describe similar experiment, evaporation model was conducted by assumption of decline water in brine with concentration of dissolved salts. PHREEQC can be inputted a variety of ion specification, temperature, pH, alkalinity and density and outputted a saturation index of feasible salts. The potential of precipitation of salts depends on saturation index which is positive or negative [15]. Therefore, it is suitable that PHREEQC can be predicted concentration of dissolved ions and salt precipitate from SWRO brine.

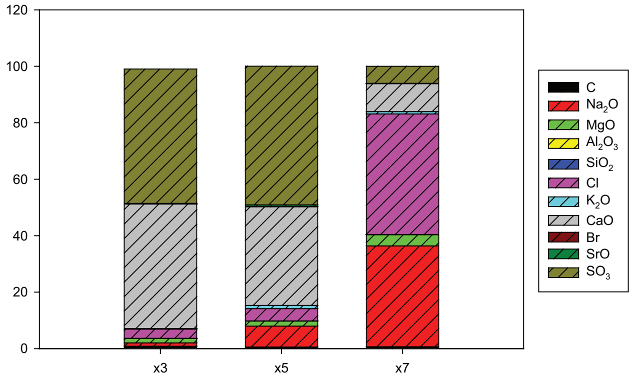

Fig. 2. Results of X-ray fluorescence (XRF) (natural).

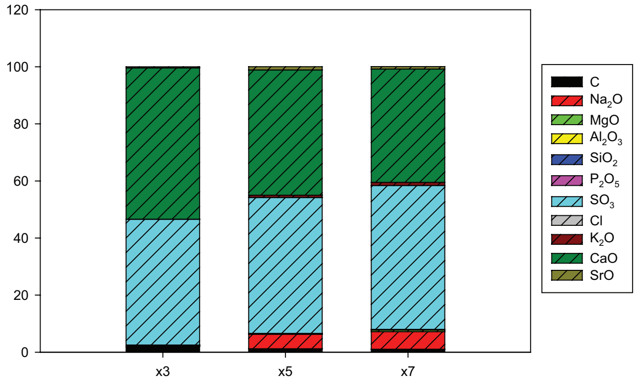

Fig. 3. Results of XRF (washed).

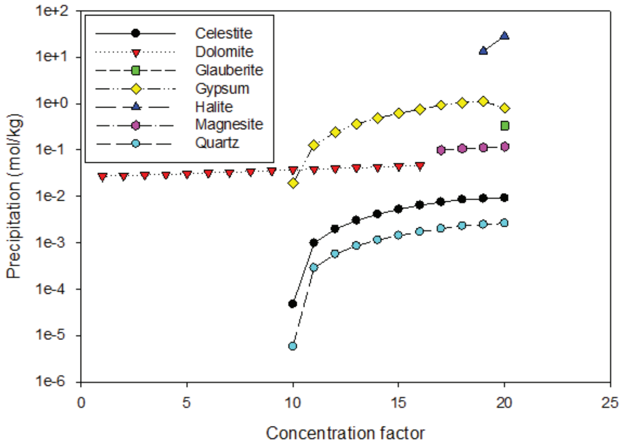

Fig. 4. Results of quantity of predicted chemical compound (PHREEQC).

3. Results and discussion

The ions of saturation indices in PHREEQC are shown in Table 2. It is indicated as a potential or possible of chemical compound by inputted ions. Since being the program performing the logK_{sp} of the saved ion in the database and precipitate (solid form) and calculation due to Gibbs free energy, PHREEQC perform the calculation to gradient of the ions concentration. The comparative results of ion concentration of filtered solution after each batch test and calculations of decreased water in SWRO brine by PHREEQC software using analyzed ion concentration of feed solution is shown in Table 3. The results of experimental and computational simulation showed the result that it is similar on the whole. The error bar graph for six kinds of target ions from dissolved in SWRO brine is shown in Fig. 1. The tendency that is increase concentration of step by step and similar to experimental and simulation result in magnesium, potassium and boron, but calcium, strontium, sodium was not. In the case of calcium, the concentration of the ions was decreased from treble concentrated and calculated results showed lower than experimental result. The sodium result was similar to magnesium, potassium and boron, but higher concentration steps of result were slightly different. The results of strontium were quite a lot of different tendencies. To identify the kind of precipitation of higher saturation concentration or co-precipitation when saturated precipitation was performed by X-ray diffractometer. The precipitated solid were found in 3, 5 and 7 times concentrated water and solid were analyzed with or without washing. The results of cleaned or not cleaned are shown in Figs. 2 and 3. By PHREEQC, calculated results from potential chemical compounds are shown in Fig. 4 and those compound formula and solubility are shown in Table 4. From X-ray diffractometer with results of calculated, the main ions into solids were Ca, Mg and Sr when it comes 3 times concentration. Among them, the major compound is gypsum ($CaSO_4$ + H_2O). Halite (NaCl) and glauberite ($Na_2Ca(SO_4)_2$) are main solids when 5 times concentration; hence we are able to found the different experimental to simulation. Previous research

Table 4
The precipitation of predicted compound by PHREEQC

Compound	Formula	Solubility
Celestite	$SrSO_4$	135 mg/L at 25°C
Dolomite	$CaMg(CO_3)_2$	106 mg/L at 25°C
Glauberite	$Na_2Ca(SO_4)_2$	–
Gypsum	$CaSO_4{:}2H_2O$	2,400 mg/L
Halite	NaCl	359,000 mg/L
Magnesite	$MgCO_3$	106 mg/L at 25°C
Quartz	SiO_2	–

Table 5
Results of calculation using proper K_{sp}

	SWRO brine	2 Times		3 Times	
	Experimental	Experimental	Calculated	Experimental	Calculated
Sr	14.4	27.0	30.16	37.0	36.78

suggests that NaCl crystal is more to be a cubic structure but there is no advantage of formation of NaCl crystal when NaCl is produced by using SWRO brine [15]. For this reason, concentration of strontium ion is drastically deceased with co-precipitation sodium chloride when sodium chloride is made of SWRO brine. However, there is different result at 3 times concentration in calculated with experimental which is affected from celestite ($SrSO_4$). The PHREEQC is calculation program of the logK_{sp} of the ion by Gibbs free energy. In case of seawater, there are a variety of dissolved ions and chloride ion which is counter ion for strontium so that K_{sp} is different at deionized water. Therefore, the K_{sp} of celestite ($SrSO_4$) should be found by trial and error method so the ideal result within error of 10% in comparison of experimental result is '$K_{sp} = –6.44$'. Table 5 shows the result by changed K_{sp}.

4. Conclusion

In this research, to evaluate potential of recovery for strontium through gradient concentration using SWRO brine was performed. The experimental results of possible ions which are magnesium, potassium and boron were similar to simulation result so it is useful to application of extraction process. On the contrary, the simulated results for calcium, strontium and sodium were different from the experimental results. Because calcium, strontium and sodium are simultaneously precipitated a sodium chloride. Furthermore, the counter ion is chloride to calcium and strontium. Hence, when performing the extraction of strontium ion using SWRO brine, the ideal concentration is under 3 times. Meantime, the tendency of calculated result by PHREEQC was similar to experimental in the majority of ions so if it is used to utilize for strontium recovery process than concentration of strontium should be under the 37 mg/L.

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