

Supporting Information of

**High-Efficiency Catalytic Wet Air Oxidation of High Salinity
Phenolic Wastewater under Atmosphere Pressure in Molten
Salt Hydrates Media**

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Table S1. The theoretical desalination efficiency of NaCl with the introduction of anhydrous CaCl₂.

Temperature (°C)	0	10	20	30	40	50	60	70	80	90	100
NaCl solubility (g/100 mL H ₂ O)	35.70	35.80	36.00	36.30	36.60	37.00	37.30	37.80	38.40	39.00	39.80
NaCl concentration (mol·L ⁻¹)	6.10	6.12	6.15	6.21	6.26	6.32	6.38	6.46	6.56	6.67	6.80
K_{sp} of NaCl	37.24	37.45	37.87	38.50	39.14	40.00	40.65	41.75	43.09	44.44	46.29
CaCl ₂ solubility (g/100 mL H ₂ O)	59.50	64.70	74.50	100.00	128.00	132.00	137.00	143.00	147.00	154.00	159.00
CaCl ₂ concentration (mol·L ⁻¹)	5.36	5.83	6.71	9.01	11.53	11.89	12.34	12.88	13.24	13.87	14.32
K_{sp} of CaCl ₂	616.09	792.14	1209.37	2924.77	6133.68	6726.87	7520.60	8552.62	9290.58	10682.02	11756.62
In the mixed CaCl ₂ -NaCl solution											
Maximum concentration of CaCl ₂ (mol·L ⁻¹)	4.37	4.89	5.86	8.34	10.99	11.35	11.81	12.36	12.72	13.36	13.80
Maximum concentration of NaCl (mol·L ⁻¹)	3.14	2.94	2.64	2.06	1.66	1.64	1.61	1.59	1.59	1.57	1.59
CaCl ₂ ion product	616.09	792.13	1209.36	2924.74	6133.59	6726.77	7520.55	8552.55	9290.45	10681.91	11756.51
Ratio of ion product to K_{sp} of CaCl ₂	≤1	≤1	≤1	≤1	≤1	≤1	≤1	≤1	≤1	≤1	≤1
Desalination efficiency (%)	48.61	51.91	57.15	66.87	73.52	74.02	74.73	75.44	75.71	76.43	76.62

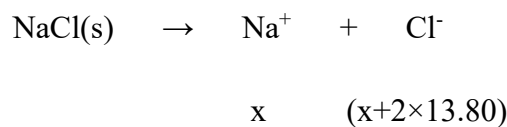
Theoretical maximum desalination efficiency of NaCl at 100 °C

$$C_{\text{NaCl, saturation}}=6.80 \text{ mol}\cdot\text{L}^{-1}, C_{\text{CaCl}_2, \text{ saturation}}=14.32 \text{ mol}\cdot\text{L}^{-1}$$

$$K_{\text{sp, NaCl}}=[\text{Na}^+]\times[\text{Cl}^-]=46.29, K_{\text{sp, CaCl}_2}=[\text{Ca}^{2+}]\times[\text{Cl}^-]^2=11756.62$$

When anhydrous CaCl_2 is introduced into a saturated NaCl solution, the solubility of NaCl in the mixed solution would decline owing to the common-ion effect, and the residual NaCl concentration could be calculated based on the amount of CaCl_2 added. Before ion product of CaCl_2 reaches up to the maximum ($K_{\text{sp, CaCl}_2}$), the introduced CaCl_2 could dissolve completely. As the ion product of NaCl ($K_{\text{sp, NaCl}}$) is smaller than that of CaCl_2 , part of the NaCl will be salted out so that the ion product of dissolved NaCl equals to $K_{\text{sp, NaCl}}$. Based on this assumption, the maximum desalination efficiency of NaCl can be calculated. By calculation, the maximum CaCl_2 concentration was about $13.80 \text{ mol}\cdot\text{L}^{-1}$, and the residual NaCl concentration was $1.59 \text{ mol}\cdot\text{L}^{-1}$, which is corresponding to a maximum desalination efficiency of 76.62% of NaCl . The detailed calculation is shown as follows.

Assuming that the residual NaCl concentration is $x \text{ mol}\cdot\text{L}^{-1}$ when the maximum Ca^{2+} concentration reaches to $13.80 \text{ mol}\cdot\text{L}^{-1}$, then the following relation remains at equilibrium state at 100°C .



$$x\times(x+2\times 13.80)=46.29 \quad \text{Eq. (1)}$$

where 46.29 is the $K_{\text{sp, NaCl}}$ at 100°C .

It turns out from *Eq. (1)* that $x=1.59 \text{ mol}\cdot\text{L}^{-1}$, and the desalination efficiency of NaCl is calculated as 76.62% $[(6.80-1.59)/6.80\times 100\%=76.62\%]$. Therefore, the theoretical maximum desalination efficiency of NaCl at 100°C is 76.62%.

Experimental verification of maximum desalination efficiency of NaCl at different temperature

In order to verify the maximum desalination efficiency, anhydrous CaCl_2 was introduced into the saturated NaCl solution at different temperature to salt out the dissolved NaCl (Table S2). Taking the desalination process at $100\text{ }^\circ\text{C}$ as an example, a saturated NaCl solution was firstly prepared by dissolving 39.8 g NaCl into 100 mL H_2O . Then, slightly excessive anhydrous CaCl_2 was added. With the introduction of CaCl_2 , a portion of dissolved NaCl was salted out gradually. After centrifuge, the salted-out NaCl as well as the undissolved CaCl_2 was collected, dried and weighted (about 31.47 g). Then, taking the mixture into a conical flask, sufficient water was added to completely dissolve the mixed salts of NaCl and CaCl_2 . To precipitate the Ca^{2+} , Na_2CO_3 was added converting CaCl_2 to CaCO_3 . The resultant CaCO_3 precipitate was collected by filtration and drying to constant weight (about 1.69 g). By this way, the mass of salted-out NaCl was calculated by difference method (29.59 g). Therefore, the maximum desalination efficiency of NaCl at $100\text{ }^\circ\text{C}$ was determined as 74.35%, which is in good agreement with the theoretical result (76.62%).

Table S2. The measured desalination efficiency of NaCl with the introduction of anhydrous CaCl₂.

Temperature (°C)	0	10	20	30	40	50	60	70	80	90	100
Volume of H ₂ O (mL)	100	100	100	100	100	100	100	100	3100	100	100
Introduced NaCl (g)	35.70	35.80	36.00	36.30	36.60	37.00	37.30	37.80	38.40	39.00	39.80
Introduced CaCl ₂ (g)	59.50	64.70	74.50	100.00	128.00	132.00	137.00	143.00	147.00	154.00	159.00
Mixture precipitation (g)	14.16	17.87	18.92	25.64	27.98	29.37	26.57	29.84	29.56	30.19	31.47
Mixture precipitation was dissolved again, and Na ₂ CO ₃ was introduced until no more CaCO ₃ precipitation formed.											
CaCO ₃ precipitation (g)	0.37	1.34	1.91	2.45	2.91	2.51	1.47	1.88	1.49	1.59	1.69
Undissolved CaCl ₂ (g)	0.41	1.49	2.12	2.72	3.23	2.79	1.63	2.09	1.65	1.76	1.88
Salted-out NaCl (g)	13.75	16.38	16.80	22.92	24.75	26.58	24.94	27.75	27.91	28.43	29.59
Desalination efficiency (%)	38.51	45.76	46.67	63.14	67.62	71.85	69.86	73.43	72.67	72.89	74.35

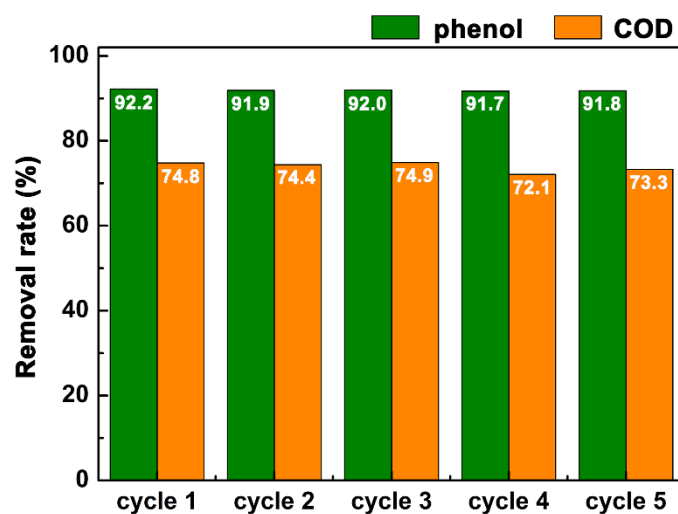


Figure S1. The removal rates of phenol and COD under the catalysis of CeCl_3 catalyst in the recycle runs after reacting at $150\text{ }^\circ\text{C}$ for 3 h in $\text{CaCl}_2 \cdot 3\text{H}_2\text{O}$ medium. Reaction conditions: 0.01 mol of CeCl_3 catalyst, 1.5 mol of CaCl_2 and 80 mL of phenol solution ($30\text{ g}\cdot\text{L}^{-1}$)

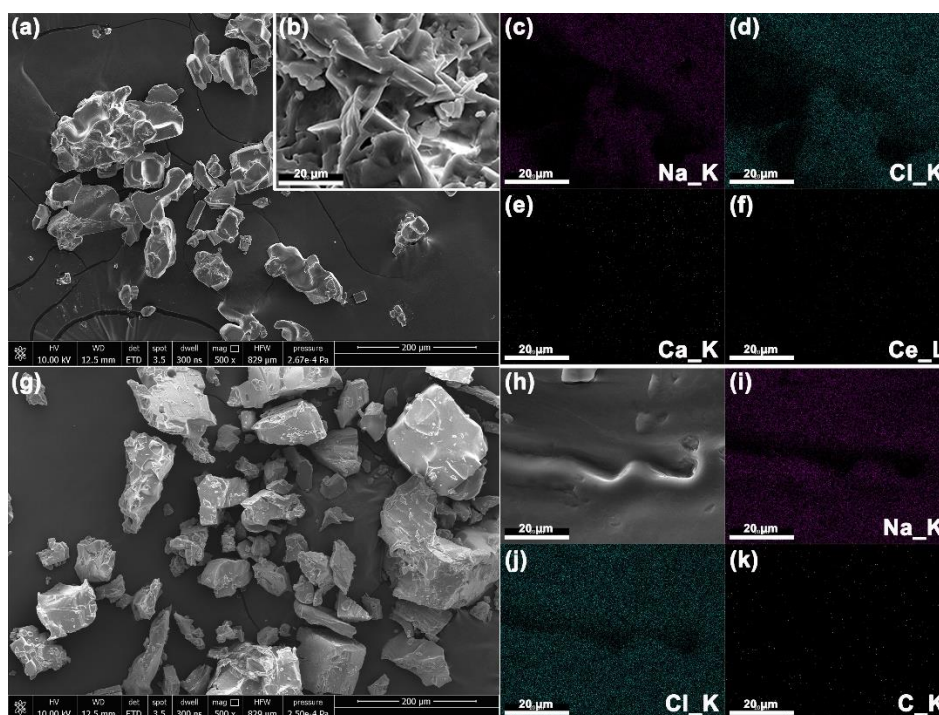


Figure S2. The SEM-Mapping images of (a~f) the NaCl obtained from direct evaporation of the wastewater to dry and (g~k) the NaCl salted-out from the wastewater owing to common-ion effect in continuous operation.