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 $CaCl_2$.

Temperature (℃)	0	10	20	30	40	50	60	70	80	90	100
NaCl solubility (g/100 mL H_2O)	35.70	35.80	36.00	36.30	36.60	37.00	37.30	37.80	38.40	39.00	39.80
NaCl concentration ($mol \cdot L^{-1}$)	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_2O)	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 ($mol \cdot L^{-1}$)	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 $CaCl_2$ ($mol \cdot L^{-1}$)	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 ($mol \cdot L^{-1}$)	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 ℃

$C_{NaCl,\ saturation}$=6.80 mol·L^{-1}, $C_{CaCl2,\ saturation}$=14.32 mol·L^{-1}

$K_{sp,\ NaCl}$=[Na^+]×[Cl^-]=46.29, $K_{sp,\ CaCl2}$=[Ca^{2+}]×[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 ($K_{sp,\ CaCl2}$), the introduced $CaCl_2$ could dissolve completely. As the ion product of NaCl ($K_{sp,\ NaCl}$) 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 $K_{sp,\ NaCl}$. Based on this assumption, the maximum desalination efficiency of NaCl can be calculated. By calculation, the maximum $CaCl_2$ concentration was about 13.80 mol·L^{-1}, and the residual NaCl concentration was 1.59 mol·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 mol·L^{-1} when the maximum Ca^{2+} concentration reaches to 13.80 mol·L^{-1}, then the following relation remains at equilibrium state at 100^{o}C.

$$\begin{array}{ccccc} NaCl(s) & \rightarrow & Na^+ & + & Cl^- \\ & & x & & (x+2\times13.80) \end{array}$$

$$x\times(x+2\times13.80)=46.29 \qquad \textit{Eq. (1)}$$

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

It turns out from *Eq. (1)* that x=1.59 mol·L^{-1}, and the desalination efficiency of NaCl is calculated as 76.62% [(6.80-1.59)/6.80×100%=76.62%]. Therefore, the theoretical maximum desalination efficiency of NaCl at 100 ℃ 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 ℃ 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 ℃ 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 $CaCl_2$.

Temperature (℃)	0	10	20	30	40	50	60	70	80	90	100
Volume of H_2O (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_2CO_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

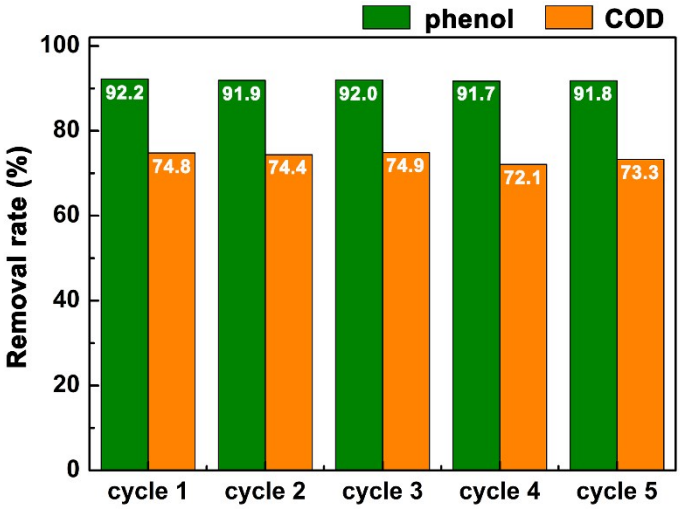

Figure S1. The removal rates of phenol and COD under the catalysis of $CeCl_3$ catalyst in the recycle runs after reacting at 150 °C for 3 h in $CaCl_2 \cdot 3H_2O$ medium. Reaction conditions: 0.01 mol of $CeCl_3$ catalyst, 1.5 mol of $CaCl_2$ and 80 mL of phenol solution (30 $g \cdot L^{-1}$)

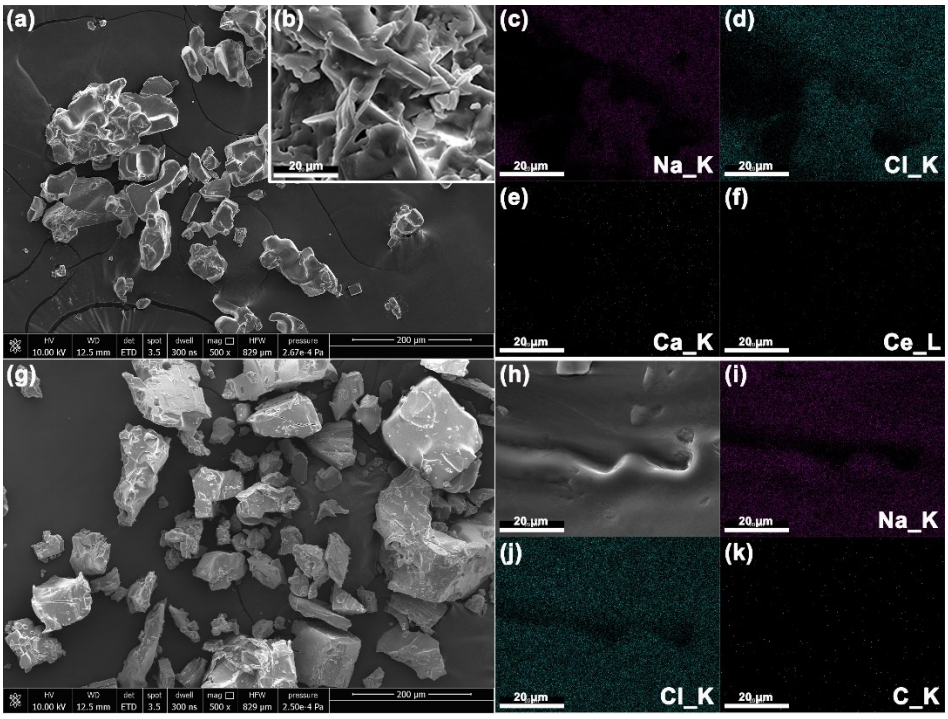

Figure S2. The SEM-Mapping images of (a~f) the NaCl obtained from direct evaporation of the wastewater to dry and (g~k) the NaCl salted-out from the wastewater owing to common-ion effect in continuous operation.