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Solubility of Sodium Chloride in Dry Steam

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The sodium ion content of dry steam that has been passed through a bed of sodium chloride has been determined for several temperatures between 400 and 550 °C and for molar volumes between 0.46 and 4.3 L mol^{-1}. Linear isotherms have been found over the entire range covered. Although measurements of pH and chloride indicated that some hydrolysis occurred, the amount of sodium chloride in the steam could be estimated within 20% from the concentration of sodium ion. Extrapolation of the data to conditions typical of Wilson lines in the low-pressure turbines of power plants yielded values of the order of parts per trillion and lower, a factor of 10^3 smaller than the value attainable by current water purification technology.

Introduction

In recent years two major equipment failures in power plants occurred. Field studies (*1*) showed that there was severe damage in the low-pressure turbine (LPT) due to stress corrosion cracking (SCC), induced by the deposition of sodium compounds such as sodium chloride, sodium carbonate, and sodium sulfate. Presumably these compounds had been introduced into the turbine system as impurities in the boiler water and were transported by the steam that powered the turbines and later precipitated.

In order the implement measures aimed at minimizing or eliminating the deposition of impurities in the LPT, it is important to know their solubilities in steam at the pressures and temperatures corresponding to those of the Wilson line (WL) where deposits are usually found. Unfortunately, no research group has been successful in measuring the solubility of sodium chloride in dry steam at those relatively low pressures and temperatures. Instead, predictions have had to be based upon extrapolations from solubilities measured at much higher temperatures and pressures. For example, in the case of a nuclear plant, the WL is typically located at 0.53 MPa (77 psi) and 143 °C. For a fossil fuel plant, the WL is typically near 0.12 MPa (17 psi) and 114 °C (*2*). In contrast, data used to predict the solubility of sodium chloride at the WL were obtained by several independent laboratories above 5.2 MPa (750 psi) and 350 °C (*3*–*7*).

Usually, those data were obtained at a variety of combinations of temperature and pressure which were then fitted to an equation of the type

$$\log S = m \log V + HT^{-1} + B \qquad (1)$$

where S is the solubility of sodium chloride expressed in parts per billion (ppb) of sodium ion; V is the molar volume of steam in L mol^{-1}; T is the absolute temperature; and m, H, and B are constants. Unfortunately, differences in the values reported for the same ranges of pressure and temperature disagree by several orders of magnitude when extrapolated to the WL conditions.

As an illustration, the predicted values for sodium chloride at the WL when using the solubility equation reported by Styrikovich (*3*) are 1.8 parts per trillion (ppt) and 2.5×10^{-3} ppt for the nuclear and fossil plants, respectively. However, the corresponding values reported by Lindsay (*8*), who fitted the solubility data reported by Sourirajan and Kennedy (*4*), were 64 and 10 ppb. In the latter equation, the slope of the solubility isotherms is obviously much smaller and values of the solubilities much higher than in the Styrikovich case.

The discrepancy in the predicted solubilities presents quite a dilemma to utility operators and equipment designers as well, since it is possible to infer quite different conclusions from them. For instance, if the ppb values are correct, current water purification technology should be able to keep the level of sodium chloride in steam low enough to avoid supersaturation of the steam by sodium chloride, followed by deposition. On the other hand, if ppt and lower concentrations are correct, supersaturation of the steam and deposition of sodium chloride could not be prevented by using current equipment and technology.

Further doubts arise about the accuracy of the predicted solubilities from the assumption made concerning the applicability of the chemical model used to fit and extrapolate the data. For example, the model assumes that the hydration number m in the equilibrium reaction

$$\mathrm{NaCl(s)} + m\mathrm{H_2O} \rightarrow \mathrm{NaCl}\cdot m\mathrm{H_2O(v)}$$

remains constant over the entire range of steam concentration. However, Martinova (*5*) reported that m gradually changed from 3.66 to 0.18 as the molar volume of steam changed from 0.36 to 2 L mol^{-1} in the temperature range of 350–600 °C. In contrast, data obtained by another research group (*7*) in the same general ranges of temperature and molar volume did not show the changes reported by Martinova.

The present study was undertaken in an effort to clarify the two major uncertainties described above. In addition, a brief evaluation was made of the extent of hydrolysis, which had not previously been made below 600 °C (*9*).

Experimental Section

The apparatus utilized to generate steam saturated with sodium chloride at a known pressure and temperature and the analytical procedures have been described elsewhere (*10*). Briefly, the approach employed a liquid-chromatographic pump, capable of operating accurately and precisely at high pressures, to feed degassed water to a preheater that converted it to steam. The steam then passed through a bed of sodium chloride crystals where equilibrium was attained.

At the part per million (ppm) level, steam was condensed continuously and, after passage through a pressure-reducing valve, was fed continually to a flame photometer for quantitative measurement of the sodium content. For concentrations of sodium chloride in steam of 200 ppb or less, an attractive alternative involved preconcentration of the sodium ion by adsorption onto a clean, hot wall of Inconel 600. Later, the sodium ion was desorbed by using condensate formed by allowing the wall to cool down.

The method depends upon the observation that, once a hot wall had the equivalent of 80 monolayers of sodium ion deposited on it (calculated on the basis of a geometrically flat surface), further deposition was negligible. At intermediate fractions of coverage, removal of sodium ion from steam was, of course, intermediate between "complete" and negligible. The method is also based on the assumption that the measurements of sodium ion reflect the contents of sodium chloride in steam.

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Table I. Effects of Column Length and Flow Rate of Steam on the Concentration of Sodium Ion

temp, °C	press., MPa	density of steam, g mL^{-1}	salt column length, m	column void volume, mL	flow of steam, g h^{-1}	time of contact, s	Na$^+$ concn, ppm
500	6.89	0.021	3.6	20	8.4	180	0.23 ± 0.02
500	6.89	0.021	3.6	20	86	18	0.22 ± 0.02
450	10.34	0.035	4.6	25	120	26	0.97 ± 0.03
450	10.34	0.035	4.6	25	88	36	0.97 ± 0.02
450	10.34	0.035	4.6	25	30	105	0.98 ± 0.01
450	10.34	0.035	6.0	33	60	70	0.98 ± 0.01
450	10.34	0.035	6.0	33	12	346	0.98 ± 0.01

Table II. Amount of Sodium Ion Deposited as a Function of the Amount of Steam Passed

deposition time, h	amount of steam passed through tubing, g	amount of sodium ion deposited, μg
1	88	27 ± 1
3	230	38 ± 2
5	400	55 ± 6
8	640	70 ± 1
13	1030	71 ± 6

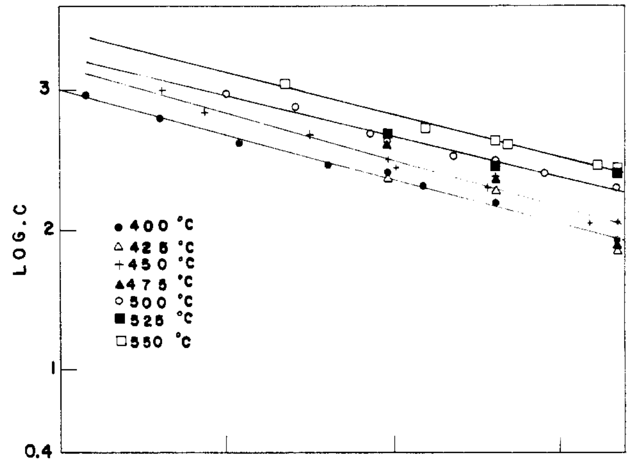

Figure 1. Solubility isotherms of sodium ion in steam at temperatures ranging from 400 to 550 °C and at molar volumes ranging from 0.46 to 0.96 L mol^{-1}.

Measurements of sodium ion in the condensate were made at different combinations of pressure and temperature. The temperatures range from 400 to 550 °C over a pressure range from 10.34 to 1.38 MPa. A total of 48 combinations were obtained, and each usually represented the average of five runs that were obtained in such a way that each one had as different a previous history as practical. For example, at a given temperature, one set of measurements was made in the order of increasing pressure and then at a decreasing series of pressure. Next, changes in temperature were performed in a similar fashion in that one series of runs was made when the temperature of successive isotherms increased while in another the temperature was decreased. Also when the temperature was changed, the system was allowed to stabilize with respect to the amount of adsorbed sodium since the capacity was temperature dependent, as described elsewhere (*10*). That stability was usually achieved by allowing steam to pass through the system overnight, especially when the temperature was being changed upward.

The pH measurements were made on-line by means of a flow-through polycarbonate plastic cell containing a combination of pH electrode. The flow-through cell was purged by a continuous flow of helium in order to displace the air, hence minimizing contamination of the solution by carbon dioxide. Calibration of the electrode was made with two buffer solutions at pH 7.00 and 4.01 according to the procedures given by the manufacturer (*11*).

Chloride analyses were made off-line by using discrete aliquots of the eluant by the mercuric thiocyanate spectrophotometric method and following the procedures given by Vogel (*12*).

Results

Preliminary Studies. This method is based on the assumption that equilibrium is attained between sodium chloride and dry steam. As shown in Table I, changing the column length from 3.6 to 6.0 m and the flow rate from 8.4 to 120 g h^{-1} did not have a significant effect upon the concentration of sodium ion found in steam. Hence, equilibrium was indeed attained.

During the flow-rate study, a 4.6-m column of sodium chloride, when retained by a 20-μm frit, produced a 0.17-MPa pressure drop at 30 g h^{-1} of steam whereas, at 120 g h^{-1}, the pressure drop was ~0.70 MPa. Although those pressure drops were relatively unimportant at 10.34 MPa, they would be increasingly significant on going to lower overall pressures of the system. However, when the pressure was controlled at the outlet of the salt column instead of the inlet, the detrimental effects of pressure drop across the column were minimized. As an illustration, when the outlet pressure was controlled at 10.34 MPa, the sodium ion content was 0.98 ± 0.03 ppm for pressure drops of 0.17 and 0.70 MPa, respectively. On the other hand, when the inlet pressure was controlled at 10.34 MPa, the sodium ion contents were 0.91 ± 0.01 and 0.85 ± 0.02 ppm for pressure drops of 0.17 and 0.35 MPa, respectively.

The next variable to be explored was the internal dimension of the tubing between the oven and the water-cooled condenser. It was thought that the sodium ion concentration in the condensate would be higher when the internal diameter was larger or the length was shorter because there would be less opportunity for loss to the wall. However, three different sections of Inconel 600 tubing—4.6-mm i.d., 6.35-mm o.d. × 53 cm long; coiled (15-cm diameter) 0.86-mm i.d. capillary, 1.6-mm o.d. × 1.2 m long; and 1.8 m of the same diameters of coiled capillary when fitted with a nichrome (AWG 22) heating coil—gave the steady-state concentration at 450 °C and 10.34 MPa of 0.98 ± 0.01 ppm sodium ion independent of the surface area, the volume, and the configuration of the tubing. Therefore, it appeared that the inner walls of the tubing were coated with sodium ion to a point beyond which further deposition was tooo slow to be measured. To that end, experiments involving preconcentration and stripping were run as a function of time. As shown in Table II, for averages of triplicate runs at 450 °C and 10.34 MPa, the amount of further deposition after 9 h was insignificant. On the basis of that study, a minimum of 1 kg of steam at 450 °C and 10.34 MPa was passed through the system after start-up so as to saturate the walls.

Solubility Measurements. Table III and Figures 1 and 2 show the solubility data obtained, for which the relative standard deviation was usually 5% or less and was never larger than ~10%. The 48 data points were correlated by the least-squares method applied to a trivariate linear equation of the

Table III. Solubility of Sodium Chloride Expressed as Sodium Ion at Different Combinations of Pressure and Temperature

temp, °C	press., MPa	molar vol., L mol^{-1}	Na$^+$ concn, ppb
400	10.34	0.46	920 ± 10
400	9.48	0.51	624 ± 27
400	8.62	0.57	421 ± 31
400	7.76	0.65	291 ± 30
400	7.20	0.70	262 ± 16
400	6.89	0.74	206 ± 11
400	6.29	0.82	156 ± 4
400	5.39	0.96	82 ± 5
425	7.52	0.70	246 ± 16
425	6.56	0.82	192 ± 2
425	5.61	0.96	112 ± 6
450	10.34	0.51	980 ± 10
450	9.48	0.57	680 ± 27
450	8.62	0.63	475 ± 22
450	7.82	0.70	322 ± 2
450	7.76	0.71	275 ± 13
450	6.89	0.81	200 ± 14
450	6.82	0.82	243 ± 7
450	6.03	0.93	112 ± 8
450	5.84	0.96	116 ± 33
450	5.17	1.10	70 ± 5
450	4.31	1.33	36 ± 4
450	3.45	1.68	18 ± 2
450	3.10	1.87	10 ± 1
450	2.67	2.19	6.4 ± 1
450	2.24	2.62	4.6 ± 1
450	1.81	3.29	1.2
450	1.38	4.30	1.1
475	8.13	0.70	431 ± 27
475	7.09	0.82	236 ± 4
475	6.06	0.96	122 ± 6
500	10.34	0.56	935 ± 1
500	9.48	0.62	746 ± 20
500	8.62	0.69	483 ± 14
500	8.44	0.70	433 ± 10
500	7.76	0.77	342 ± 4
500	7.36	0.82	321 ± 9
500	6.89	0.87	262 ± 4
500	6.28	0.96	200 ± 6
525	8.75	0.70	435 ± 10
525	7.62	0.82	292 ± 25
525	6.50	0.96	247 ± 7
550	10.34	0.61	1114 ± 20
550	8.62	0.74	539 ± 10
550	7.89	0.82	432
550	7.76	0.83	430
550	6.89	0.94	289
550	6.72	0.96	272

Table IV. Coefficients for the Solubility Equation for Sodium Chloride

group	*m*	*H*	*B*
Sourirajan and Kennedy	−0.719	−2095	7.02
Styrikovich	−3.66	−2101	4.85
present study	−3.36 ± 0.05	−1760 ± 91	4.45 ± 0.12

same type as eq 1. Table IV shows these results and compares them with those reported by Styrikovich (*3*) and by Lindsay (*8*). It is immediately apparent that the results obtained in this work are closer to those reported by Styrikovich (*3*).

Styrikovich and Martinova (*5*) also reported that the isotherms for sodium chloride were curved in the steam molar volume range of 0.36–2 L mol^{-1} and the slopes (m) of the isotherms changed from 3.66 to 0.18 in the temperature range of 350–600 °C. In contrast, the corresponding solubility isothems in the present study for the temperature range of 400–500 °C and steam molar volumes in the range of 0.46–0.93 L mol^{-1} do not show a change in slope, as can clearly be seen in Figure 1. Furthermore, the isotherm at 450 °C, which was extended to molar volumes of ~4.3 L mol^{-1}, can be seen in Figure 2 to have no curvature.

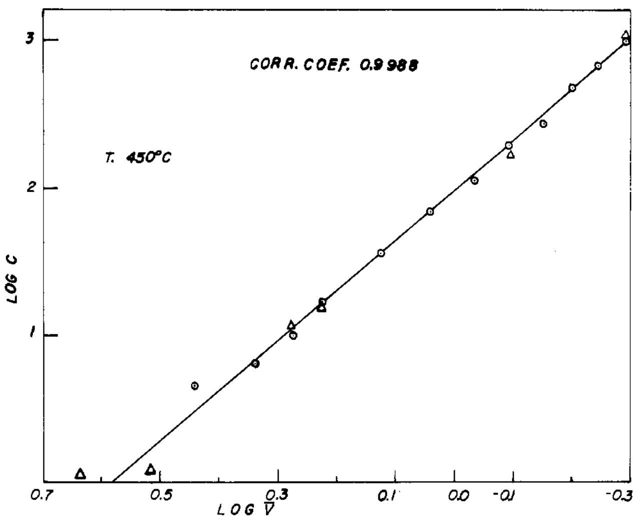

Figure 2. Solubility isotherm of sodium ion in steam at 450 °C and at molar volumes ranging from 4.3 to 0.5 L mol^{-1}.

Table V. Analyses of Steam Condensate from Runs Made at 450 °C and 10.34 Mpa ,

run	Na$^+$ concn, ppm (M)	Cl$^-$ concn, ppm (M)	pH	10^{-pH}	anion excess, %
I	1.08 (4.7 × 10^{-5})	1.96 (5.53 × 10^{-5})	5.2	0.63 × 10^{-5}	3.6
II	1.05 (4.57 × 10^{-5})	2.06 (5.81 × 10^{-5})	5.4	0.4 × 10^{-5}	14.5
III	0.96 (4.18 × 10^{-5})	1.71 (4.84 × 10^{-5})	5.4	0.4 × 10^{-5}	5.4

The discrepancy between the present data and Martinova's (*5*) may be the result of a significant pressure drop in the latter system. If the system pressure was measured near the inlet rather than the outlet of the system, significant deviations would become increasingly noticeable at relatively high molar volumes, as shown in our preliminary experiments.

Finally the validity of the assumption that measurement of the sodium ion reflected the content of sodium chloride was examined briefly at 450 °C and 10.34 MPa. When samples of condensate were analyzed for sodium ion, chloride, and hydrogen ion, the condensate was slightly acidic (pH ~5.4) and the ratio of the molar concentrations of chloride to sodium was ~1.2, as shown in Table V. Hence, some hydrolysis was occurring. In addition, the pH of the solution that had been passed through a salt-packed column that had been used in the system for several weeks yielded a highly basic solution (~pH 11). That observation confirmed the fact that some hydrolysis did occur even at a much lower temperature that had been reported. However, measurements of sodium ion reflected the solubility of sodium chloride within 10–15%, an uncertainty that is quite small in comparison to the discrepancies of up to 60-fold found in the literature (*3*, *4*).

Conclusions

The results of the present study suggest that the chemical model based on a constant value for m, the hydration number, is valid for molar volumes close to those found at the WL. This implies that solubilities at the WL are of the order of ppt and lower. For the same values of temperatue and pressure given earlier for the locations of the typical WLs, the present results extrapolate to 3.8 ± 2 ppt of sodium ion for the nuclear plant and of (14 ± 8) × 10^{-3} ppt of sodium ion for the fossil fuel plant. These values are much closer to those predictd by the Styrokovich (*3*) data than to those predicted from the Sourirajan and Kennedy data (*4*). Consequently one must conclude that, using current technology, boiler feedwater of necessary purity cannot be achieved to avoid supersaturation of the steam with respect to sodium ion present with chloride.

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Ion Exchange in Mordenite. Verification of the Triangle Rule

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Ion-exchange isotherms obtained with synthetic mordenite have been measured at 25 °C involving the cation pairs $Na^+ \rightleftarrows Li^+$, $2Na^+ \rightleftarrows Co^{2+}$, and $H_3O^+ \rightleftarrows Li^+$. In all cases the exchange was reversible. Values for the thermodynamic equilibrium constant, K_a, and the standard free energy of exchange, $\Delta G°$, were calculated for each exchange. The K_a values determined for the above exchange reactions are respectively 0.048, 0.63, and 0.0052, while the corresponding $\Delta G°$ values are 1.80, 0.14, and 3.11 kcal/equiv. These experimental K_a and $\Delta G°$ values were then compared with values derived by the triangle rule. It was determined that this rule is effective in deriving thermodynamic equilibrium constants for these reactions.

Introduction

There is interest in mordenite as a selective adsorbent in the production of oxygen-enriched air. This zeolite exhibits enhanced adsorption of nitrogen over oxygen due to a quadrupole interaction between the nitrogen molecule and the polar zeolite surface. Considerable attention has been paid to the possibilities of modifying the adsorption selectivity of zeolites. An effective method of modification is the ion exchange of the cations in the zeolite structure, which leads to changes in the adsorption energy of the adsorbate molecules.

The structure of mordenite has been elucidated by Meier (*1*) and further described by Barrer and Klinowski (*2*). Ion-exchange data have been published on the behavior of mordenite toward selected alkali and alkaline-earth metal cations and the NH_4^+ cation (*2*). Also, an investigation into transition-metal ion exchange in ammonium mordenite has been reported (*3*). The purpose of this letter is to present ion-exchange isotherms obtained with mordenite not previously published, to determine the standard free energy of these exchanges, and to compare the experimental values of $\Delta G°$ with values derived by the triangle rule (*2*, *3*).

Experimental Section

Synthetic sodium and hydrogen mordenites (sodium and hydrogen Zeolon) were supplied by the Norton Co. Analysis of the zeolites gave a Si/Al ratio for the sodium mordenite of 5.42, while that for the hydrogen mordenite was 6.65. These Si/Al ratios are indicative of alumina-deficient materials.

Either the sodium or hydrogen form, as indicated, was employed to determine the exchange isotherms of $Na^+ \rightleftarrows Li^+$, $2Na^+ \rightleftarrows Co^{2+}$, and $H_3O^+ \rightleftarrows Li^+$. The $Na^+ \rightleftarrows Li^+$ and $2Na^+ \rightleftarrows Co^{2+}$ exchanges were measured at 25 °C with total solution concentration of 0.1 N. Weighed amounts of the sodium mordenite were rotated in plastic bottles with solutions containing known quantities of the two exchanging ions. For each point on the isotherm, the bottles were rotated for 5 days. Preliminary kinetic experiments indicated that equilibrium was established in 48 h. Subsequently, the solid zeolite was separated from the solution by centrifugation. The extent of exchange was determined by monitoring the change in solution concentration before and after exchange. Isotherm points were also measured in the reverse direction so that ion-exchange reversibility could be demonstrated.

The $H_3O^+ \rightleftarrows Li^+$ exchange was measured in stepwise fashion using a procedure developed by Barrer and Klinowski (*4*). A weighed amount of hydrogen mordenite (pretreated with acetic acid to ensure the absence of sodium) was added to a solution of 0.05 N LiCl and rotated at 25 °C for 2 days. Kinetic experiments indicated that equilibrium was reached in less than 24 h. The zeolite was then separated from solution by centrifugation, and the extent of exchange was again determined by solution analysis. Additional isotherm points were obtained by adding fresh LiCl solutions to the partially exchanged zeolite. Lithium mordenite was back-exchanged into the hydrogen form, also in steps, by using 0.04 N acetic acid solutions.

Results and Discussion

The experimental isotherms are shown in Figures 1-3. The subscript c denotes the equivalent fraction of the given ion in the zeolite crystal, while the subscript s indicates the equivalent fraction of the given ion in solution.

The thermodynamic equilibrium constant, K_a, was evaluated graphically by calculating the area under the curve obtained by plotting the logarithm of the rational selectivity coefficient vs. the ionic composition in the zeolite (*5*). Plots for the cobalt exchange were calculated from normalized ion-exchange isotherms because the equivalent fraction of cobalt in the crystal never reached unity (*3*). Finally, the standard free energy of