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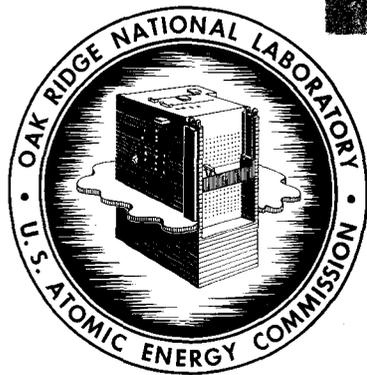
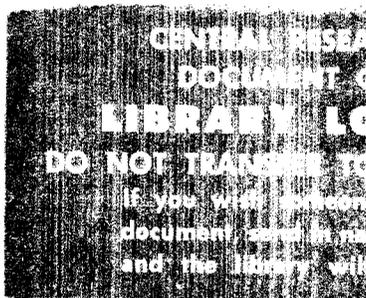
ORNL-2984
UC-70 - Radioactive Wastes

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WASTE DISPOSAL IN SALT:

I. THE HNO_3 - NaCl REACTION

H. Kubota
T. Tamura



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ORNL-2984

Contract No. W-7405-eng-26

HEALTH PHYSICS DIVISION

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Hisashi Kubota and Tsuneo Tamura

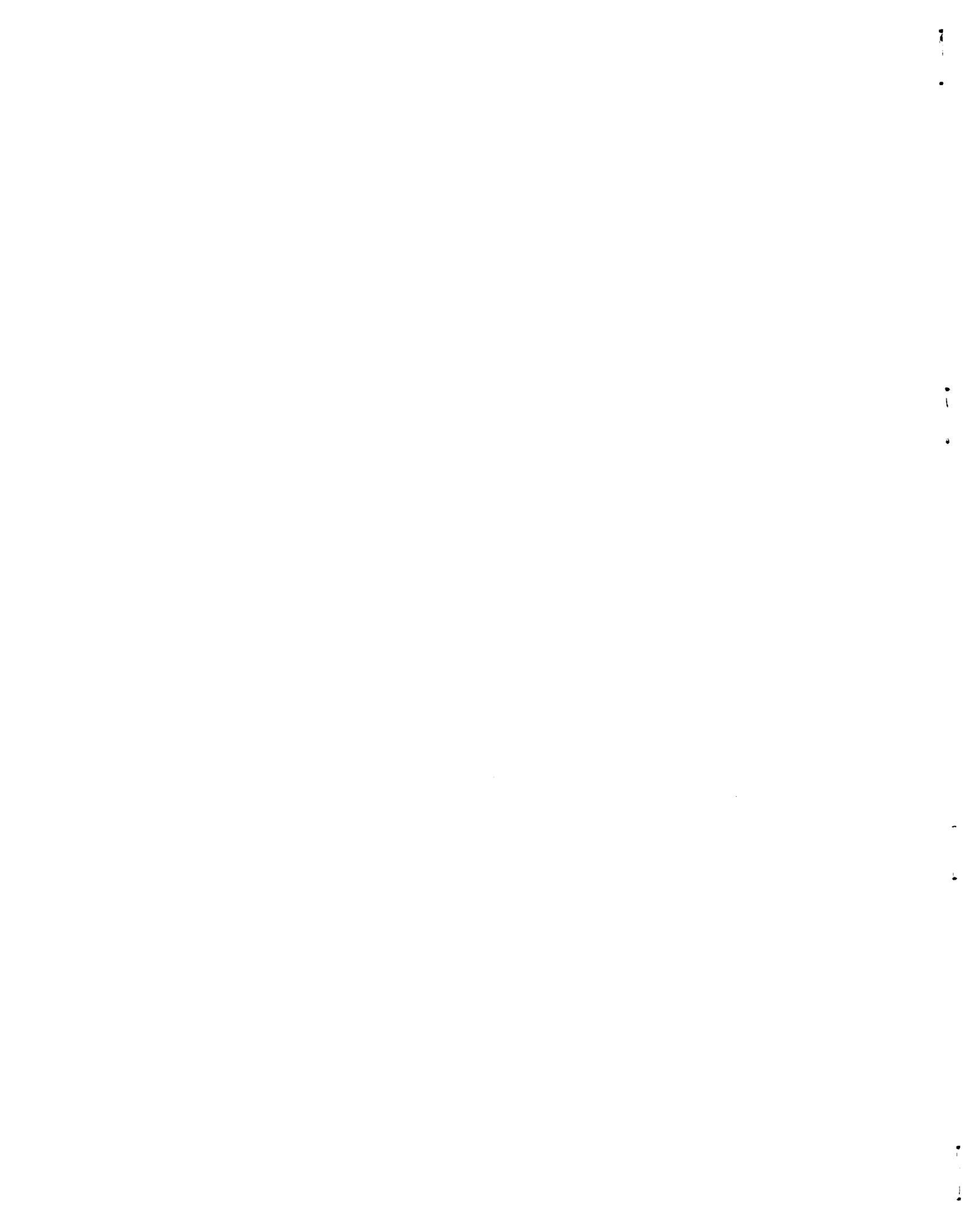
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ABSTRACT

The chemical reaction between nitric acid and sodium chloride was investigated in order to provide preliminary information for subsequent studies on the interaction between simulated Purex waste solution and salt. The reaction is characterized by the production of chlorine and nitrosyl chloride and can be considered to be the same as the aqua regia reaction. Within the limits of the conditions imposed by the projected field studies, the acid concentration and temperature are the two parameters which control the extent of the interaction.

THE REACTION BETWEEN ACID PUREX WASTE SOLUTION AND SALT

The possibility of storing liquid radioactive waste products from nuclear reactor fuel reprocessing plants in salt mines has been proposed,¹ and feasibility studies are now under way. The advantages of natural salt as a disposal medium have been discussed in another publication.² This paper is concerned with the laboratory tests that were conducted to study the reactions that could be expected when an acid waste solution is stored in salt.

This study was limited to nonradioactive solutions. A few assumptions were necessary in order to assure results that could be compared with those from field experiments. First of all, the radioactive waste solutions were assumed to attain a temperature of 80° C as a direct consequence of the decay of fission products. This maximum temperature would be expected to prevail for several months before total activity began to decrease. The second assumption was that the solution was to be contained in essentially a closed system where any gaseous products would be in direct contact with the surface of the solution, and liquid would not be boiled away. The pressure, however, was to be atmospheric, implying that product gases would be bled off to maintain constant pressure.

EXPERIMENTAL

Acid Purex waste solution is normally about 7 M in total acid. The predominant anion is nitrate, and the only other anion of any consequence is sulfate which is usually not more than 0.5 M. A nearly equivalent amount of

iron (III) is present, plus small to trace quantities of the fission products. In these studies any reactions or effects due to the sulfate, iron, or trace materials were neglected and the study was confined to the nitric acid-sodium chloride system.

The reactions were carried out in 3-neck boiling flasks of one liter capacity. A thermometer to measure solution temperature was seated in one of the side necks. The other side neck held a thermometer to measure the vapor phase temperature for gas evolution study, and a liquid sampler during the solution studies. The liquid sampler was a pipet of about two ml capacity fashioned from a 19/38 standard taper through joint. The standard taper joint made it possible to keep the barrel of this sampler always dipping in the solution between sampling so that no separation of salt would occur during the sampling process. A standard taper fitting topped by a female 12/5 ball joint was inserted into the center neck for gas collection. Gas samples were collected in 250 ml gas sampling bottles which were tipped on one end with a male 12/5 ball joint for easy coupling to the sampling port. An air reflux condenser fashioned from 10 mm I.D. glass tubing 75 cm long was attached to the center neck for the solution studies. The flask was heated with a heating mantle, and the rate of heating was controlled by a Variac. In the solution studies reported in the later sections of this report the flask was heated in an oil bath to give a more even distribution of heat within the solution.

Gas samples were analyzed on a gas chromatograph for chlorine and nitrosyl chloride. Because the peaks for other gases such as the nitrogen oxides and carbon dioxide, which could presumably be present under actual conditions,

overlapped that of nitrosyl chloride, the gases were scanned on an infrared spectrometer for qualitative and quantitative determinations of the above named constituents.

Solution samples were taken into tared weighing bottles, weighed, and diluted to 50 ml. with water. Aliquots of the diluted solutions were used for the analyses. The analyses are reported on a weight basis (molal). The acidity was determined by titration with standard sodium hydroxide using a mixed methyl red-brom cresol green visual indicator. Chloride was titrated with standard silver nitrate after first neutralizing the acid with base. Potassium chromate indicator was used. Nitrates were first reduced with Devarda's alloy in a basic medium and distilled over as ammonia which was titrated with standard acid. Sodium was determined by flame photometry.

The Nature of the Reaction Between Nitric Acid and Salt at 80° C

Seven hundred ml. of 7 M nitric acid were heated to 85° C in the flask. When the solution attained the required temperature, 250 grams of preheated sodium chloride were added very quickly. There was a drop in temperature when the two ingredients were mixed, and the temperature became very close to 80° C. The gases that were evolved were trapped in a 250 ml. gas sample bottle held in a vertical position such that the evolved gases displaced the air originally present in the sample bottle by upward diffusion. The time that was necessary for collection was proportional to the relative activity of the reaction that generated the gases. The sample was then analyzed. The relative quantities of evolved gases are given in the following table.

Table 1

Relative Quantities of Gases Evolved by the Reaction
Between HNO_3 and NaCl

<u>Interval After Start of Reaction</u>	<u>Mol Per Cent</u>		<u>Unidentified</u>
	<u>Cl_2</u>	<u>NOCl</u>	
0-10 min.	48.1	39.8	
20-35 min.	41.8	45.7	
1-2 hr.	42.8	46.0	
4-20 hr.	25.7	52.7	< 5

The nature and relative quantities of the gases identify this reaction as being the same as that between hydrochloric and nitric acids - the aqua regia reaction. The slight discrepancy in molar quantities of the two main gases is attributed to the greater solubility of nitrosyl chloride; the incompleteness of the analysis is due to air contamination in the flask.

The Changes in the Concentration of the Ionic Species in Solution

The changes in concentration of the principal ions in the solution were studied as a function of time. In a run similar to that presented in Table I, 7 M nitric acid and salt were reacted at 80°C , and liquid samples were taken at appropriate intervals. The sample solutions were analyzed for acid and chloride content. The changes in the concentrations of the H^+ and Cl^- ions are depicted in Figure 1. The acid value decreases fairly rapidly to a nearly constant value while the chloride value builds up to a constant value.

In order to magnify the concentration increments and still keep the reaction velocity slow enough for accurate sampling, the reaction was run at

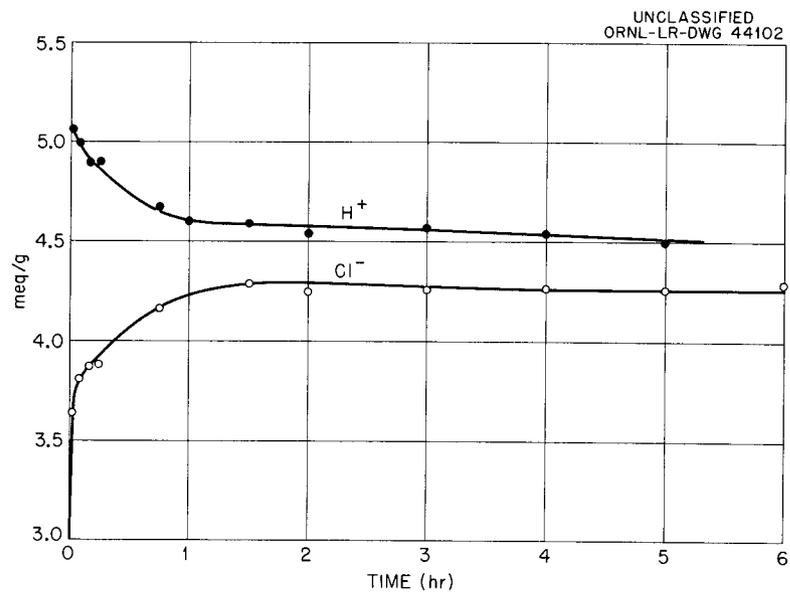


Fig. 1. The Reaction Between 7 M HNO₃ and NaCl at 80°C. Change in [H⁺] and [Cl⁻] with Time.

65° C starting with an initial acid concentration of 9 M. The time plot of the concentrations of the hydrogen, sodium, nitrate, and chloride ions are given in Figure 2. The hydrogen ion decreases along a path which looks almost exponential, and the nitrate follows a similar but less abrupt path. The sodium and chloride concentrations increase as the salt goes into solution, but the former is always more concentrated. All concentrations approach a nearly constant value after two hours. The gas analysis showed that chlorine and nitrosyl chloride were still the main products.

The Reaction Between Hydrochloric Acid and Sodium Nitrate

In order to test whether the reaction was dependent upon the ions present in the solution or upon the nature of the starting materials, the reaction was repeated using 9 M hydrochloric acid and solid sodium nitrate. The gas analysis showed that the products were still chlorine and nitrosyl chloride, thus, the principal reaction is still the same. The time plot of the acid and chloride concentrations are given in Figure 3. The acid decreases in the same manner as that in the nitric acid-sodium chloride system and approaches a nearly identical asymptotic value. The more pronounced decrease of chloride was due to the crystallization of sodium chloride from the solution.

Under the conditions of the tests there are always sufficient chloride and nitrate available for the reaction to take place. Since the hydrogen ion concentration follows the same path regardless of the relative ratio of chloride to nitrate, it was concluded that the hydrogen ion was the limiting

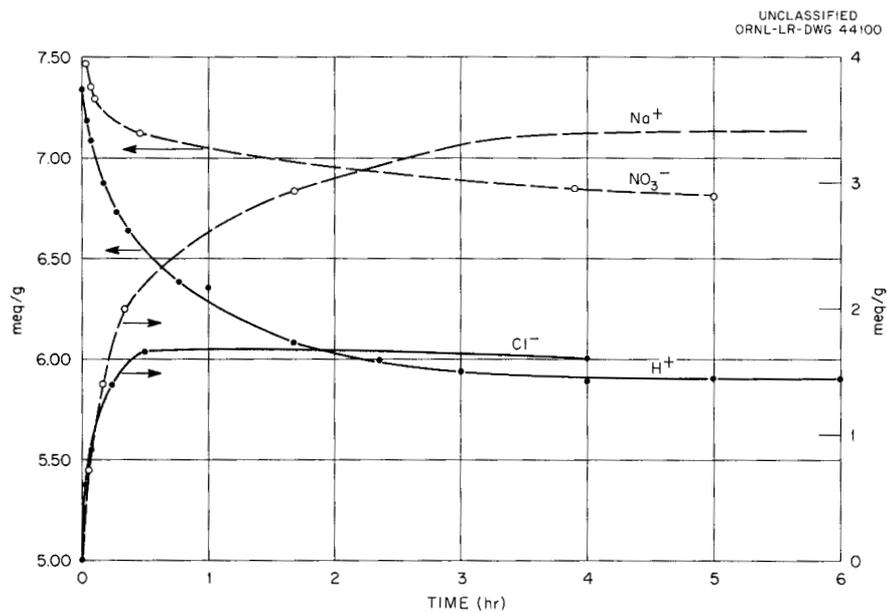


Fig. 2. Changes in Ionic Concentrations of 9 M HNO₃ with NaCl at 65°C.

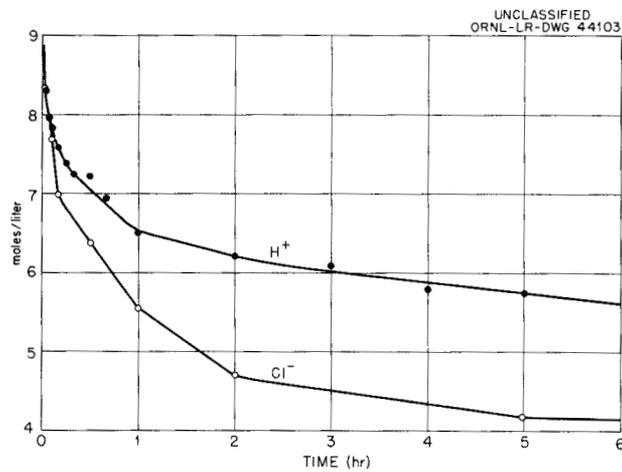


Fig. 3. Reaction Between 9 M HCl and NaNO₃.

entity that determined the extent of the reaction at any given temperature.

The Aqua Regia Reaction as a Function of Temperature

The effect of temperature upon the speed as well as the extent of the reaction was followed using 9 M hydrochloric and nitric acids in the volume ratio of 3:1. The decrease of the hydrogen ion was determined at 70, 80, 90, and 100° C. The results are graphed in Figure 4. At any given temperature, the acid value reaches a nearly constant value. The time it takes to reach this value is an inverse function of the temperature. Thus, the reaction is spent after about three hours at 70° C, two hours at 80° C, one hour at 90° C, and twenty minutes at 100° C.

The Nitric Acid-Sodium Chloride Reaction as a Function of Temperature

The temperature dependence of the nitric acid-sodium chloride system was studied next. A 9 M nitric acid-sodium chloride mixture was heated at 70° C until analysis showed that the hydrogen ion concentration had reached a nearly constant value. The temperature was then raised to 80° C and maintained at this point until the acid value was again constant. The equivalent values for 90° C and 100° C were determined in a similar manner. The data are given in Figure 5. By assuming that the density of the solutions is 1.2 g./ml., the estimated molarity of acid at which the reaction ceases at each of the temperatures investigated is as follows:

<u>70° C</u>	<u>80° C</u>	<u>90° C</u>	<u>100° C</u>
7.4	6.5	5.2	4.0

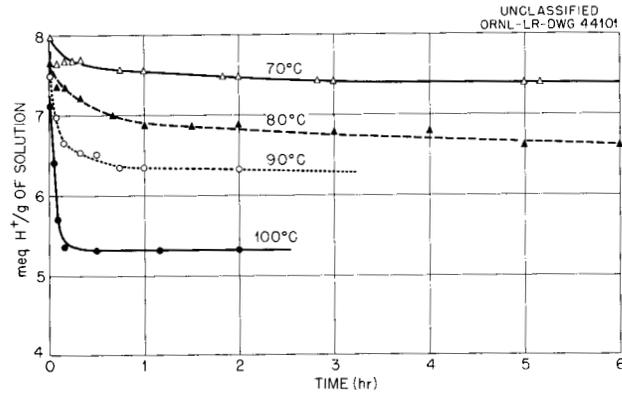


Fig. 4. The "Aqua Regia" Reaction as a Function of Temperature.

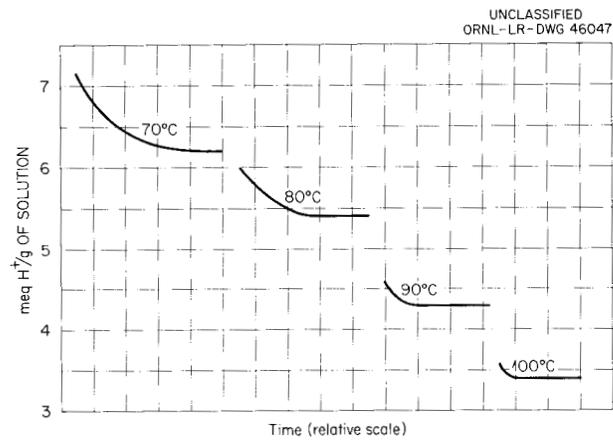


Fig. 5. The HNO₃-NaCl Reaction as a Function of Temperature.

Further assuming that the aqua regia reaction



is the principal reaction it is possible to estimate the total gas production that can be expected from a waste solution that is originally 7 M in acid at each of the temperatures. The values are given in Table 2.

Table 2

Total Gas Production from 7 M HNO₃-NaCl System

<u>Temperature</u> °C	<u>Acid Consumed</u> Eg./liter	<u>Volume of Gas Produced</u>	
		<u>liters/liter soln.</u>	<u>Cubic ft./gal.</u>
70	---	---	---
80	.50	6	.58
90	1.8	20	1.9
100	3.2	36	3.5

DISCUSSION

The work described above was limited to a pure nitric acid-sodium chloride system. If these results are to be extended to actual field conditions, no major change in solution behavior and gas production are expected. The hydrogen ion concentration and temperature will still be the two parameters that determine the degree of reaction.

There are, however, some considerations that seem pertinent. Aqua regia is a very strong oxidizing material which combines the high oxidizing potentials of chlorine and nitric acid together with the decreased reduction potentials of many metals in this mixed system such that very few metals are resistant

to its action. When free metals react with aqua regia, nitrogen dioxide, nitric oxide, nitrous oxide, or even ammonia can be formed depending upon the potentials involved. The very resistant Haynes "Stellite" material that is being used as cover material in the field experiments is slightly attacked and both nitrogen dioxide and nitrous oxide are produced.

Natural salt contains many impurities chief of which are shale, carbonates, anhydrite, and organic matter. Shale often contains small amounts of ferrous iron which is oxidized to ferric by nitric acid with the associated formation of oxides of nitrogen. The reaction between carbonates and acids release carbon dioxide while anhydrite is unaffected. The extent to which organics react depends upon the functional groups present. The end products are carbon dioxide and oxides of nitrogen.

An investigation was made to determine the presence of reactive materials in the diggings from the experimental pits at the Hutchison Mine. Of the samples taken from the pit profile only shale evolved nitric oxide. Carbon dioxide was obtained from both shale and from predominately anhydrite strata.

There is a major difference between these laboratory tests and the field tests. In the laboratory the components were mixed after each had been brought up to the maximum temperature. In the field experiments the solutions were saturated with salt at a room temperature prior to placement in the salt pits.

When a hot liquid sample is allowed to cool, some salts separate from the solution which makes it difficult to use molar concentrations. The molal system, therefore, was selected, and the results are expressed in terms of

unit weight of solution. This allows the study of relative changes taking place within the solution with minimum error. There can be considerable error in converting from the molal to the molar system by assuming a constant density for all the solutions at all the temperatures studied. As a result, there is a large uncertainty in the values that are given Table 2 where the gas volumes have been calculated on the basis of molar values converted from molal values assuming a constant density. A program is now under way to make direct measurements of gas production and correlate them with molar changes in acidity.

The thermochemistry of the aqua regia reaction shows that the reaction is endothermic to the extent of over forty kilocalories for the balanced molar equation. This cooling phenomenon is evident when the salt and acid are mixed.

The results indicate two possible directions that can be taken in acid waste disposal. If heat removal is the prime problem and gas production a minor one, a very high initial acid concentration will help consume a great proportion of the generated heat. On the other hand, if heat can be adequately siphoned off the surrounding salt and the production of gases is the major problem, the lowering of the hydrogen ion concentration should provide a means of effectively reducing gas production.

SUMMARY

The reaction between nitric acid and sodium chloride can be considered to be essentially the same as that between nitric and hydrochloric acids.

The chief products are the strongly oxidizing gases chlorine and nitrosyl chloride. Within the conditions imposed by the acid waste-salt system the hydrogen ion concentration is the critical ionic entity that limits the degree of reaction. The extent of the reaction is also dependent upon the temperature of the system. There is an acid value for each temperature in the range 70-100° C which is the acidity at which the rate of reaction decreases to the point that gas production is negligible.

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