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BROOKHAVEN NATIONAL LABORATORY
MEMORANDUM

January 30, 1959

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Ronald J. Brown PNNL ADD
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To: B. Manowitz
From: M. Steinberg and L. Slater
Subject: Monthly Progress Report
Waste Processing Studies
January 1959

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Removal and Recovery of Xe-Kr (M. Steinberg)

A test for studying the radiation decomposition of Freon-12 when in contact with Kr-85 activity and its corrosive action on materials of construction, was completed during the past month. About 40 cc of liquid F-12 at room temperature (20 to 30°C) was contacted with the following mixture of gases in a closed vessel:

7.5cc Kr (7% Kr-85) - 0.75 curies

10.0cc Xe

10.0cc Air

The above composition and concentration simulate the conditions assumed to exist in the top of the noble gas stripping tower, with the exception that the temperature and pressure in the test were higher. The top of the stripping tower after the condenser operates at -70°C and 2 atm. compared to the test temperature of 20 to 30°C and 6 atm. The test conditions were therefore much more severe than would be encountered in practice. Samples of both mild steel and stainless steel were inserted in various sections of the test vessel. After 20 days of contacting with daily shaking, the pressure was substantially

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the same as at the beginning of the test. The Freon was removed and analyzed for halogen content and the steel specimens were weighed. The metal parts were found to be coated with a thin layer of a whitish-green deposit. The mild steel samples showed a heavier deposit than the stainless steel samples. All samples had increased in weight. Chemical analysis showed the presence of chloride. X-ray diffraction analysis showed the coating to be $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$. No fluoride was detected. Based on the weight gain the rates of corrosion due to FeCl_2 formation are given in Table 1.

Table 1

Corrosion of Steels by Freon 12 (CCl_2F_2)
in the presence of Kr-85 and Xenon,
Oxygen and Nitrogen.

Sample No.	Type	Location	Corrosion Rate I.P.Y.
1	S.S. 304	Gas	0.00030
3	"	Interface	0.00033
5	"	Liquid	0.00055
2	SAE 1020	Gas	0.00039
4	"	Interface	0.00066
6	"	Liquid	0.00097
7	S.S. 316	Gas	0.00038
8	"	Interface	0.00034
0	"	Liquid	0.00040

Although the liquid phase mild steel sample shows the most corrosion, the rate is still under 1 mil per year.

An estimate of the quantity of chlorine formed and the radiation dose gave a G value of approximately 0.8 molecules of chlorine per 100 ev. This compares with a G value of 0.31 for Freon-11 (CCl_3F) at

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-70°C obtained with the use of a beam from an electron accelerator (ORNL Cf 56-8-198). The halogen consisted mainly of chlorides with much smaller amounts of fluorine present. According to the authors, the G values should increase with increasing temperatures. This seems to be confirmed by the value derived above.

The tests carried out indicate that decomposition and corrosion rate are not serious when using Freon-12 as a process solvent for removal and recovery of the fission product noble gases. A maximum of several hundred ppm by volume of chlorine may find its way into the product gas. This can be removed in final purification along with residual oxygen and nitrogen by reactive metal scavenging.

Consideration might be given to the use of stainless steel rather than mild steel because of the lowering of the impact resistance of mild steel at temperatures below about -50°C.

Neutralized Waste Treatment (M. Steinberg)

A series of runs was undertaken for determining the decomposition of sodium nitrate at various temperatures for comparison of the extent of decomposition and causticization on addition of a causticizing agent. From 10 to 15 gm of sodium nitrate alone was heated in the reaction vessel for periods of time ranging from 2.5 to 5 hrs. The gas evolved was scrubbed with a caustic solution through two gas bubblers. A small flow of air was used to sweep the gas from the reaction vessel. The heating was discontinued when it was observed that the evolution of gas from the vessel ceased. The residue was dissolved in water and analysed for sodium hydroxide. Analysis of the wash solution indicated the amount of nitric acid recovered.

The results of this series of runs are given in Table 2 and indicate the yield of caustic and nitric acid based on stoichiometric conversion of sodium nitrate.

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Table 2

Conversion of Sodium Nitrate

Run No.	Reaction Temperature °C	NaOH Yield %	HNO ₃ Yield %
7	600	2.6	
28	600	2.5	2.1
	700	7.2	
29	700	7.7	3.4
20	725-750	4.3	
30	750	20.4	4.3
16	762-841	40.0	
31	800	61.9	0.0
32	810	62.8	4.3

The data indicate that conversions of greater than 50% of nitrate to caustic are not obtained until temperatures in the order of 800°C are reached. The low recovery of higher oxides of nitrogen as nitric acid indicate that the gases evolved consist of nitrous oxide or more probably nitrogen and oxygen. The literature indicates (J. Phys. Chem 60 256 (1956) that at temperatures above 900°C the sodium nitrate is completely vaporized. This is probably due to volatilization of Na₂O formed during decomposition. The iron oxide causticizing agent therefore definitely helps the reaction since a caustic yield of approximately 85% and a nitric acid yield in the order of 50% is obtained at 720°C. A series of experiments with iron oxide is presently being completed.

Cs and Sr Removal and Recovery (L. Slater, Problem Leader)

It was found that cesium and strontium formed polyiodides that are extractable into organic solvents of fairly high dielectric constant. Solvents used were nitromethane, nitroethane, nitrobenzene, and furfural. Aqueous phases were solutions of varying amounts of sodium iodide and iodine. Maximum NaI concentration used was 0.12M. Maximum aqueous iodine concentration was iodine saturated 0.12M NaI at room ambient temperature (~25°C), which is about 0.06M I₂. NaNO₃ was added to aqueous phases at times to give a total Na⁺ concentration of 0.5M. Equal volumes of organic and aqueous phases were used in extractions, and the organic phases were usually about 0.02M in iodine, which is about the solubility of iodine in nitromethane at room ambient temperature.

Extraction coefficients for cesium into all four solvents were quite high. Small amounts of radioactive impurities left in aqueous

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phases made extraction coefficient values obtained for cesium in many cases rather uncertain, and so are not given here. They will be given later after analysis for impurities has been completed. However, E^0_a values for cesium as high as 350 have been obtained. Radioactive impurities in the aqueous phase would tend to make the actual E^0_a for cesium even higher. $10^{-3}M$ and $\sim 10^{-7}M$ Cs gave similar results.

The ratio of I_2 to I^- is quite important in these systems. Because of the great solubility of I_2 in furfural, extraction systems employing this solvent need relatively large concentrations of I_2 in order to form extractable polyiodides in the aqueous phase.

Using tracer Na^{24} , the extraction of sodium from solutions similar to those used for cesium extractions was studied. Organic phases were the same as for cesium extractions. Separation factors of cesium from sodium as high as and over three thousand were obtained.

Under the conditions so far employed, the only solvent showing promise for the extraction of strontium is furfural. E^0_a for the extraction of both tracer Sr^{90} ($\sim 10^{-7}M$) and natural strontium ($0.001M$) from a solution $0.12M$ in NaI and saturated with I_2 at room ambient temperature ($\sim 0.057M$) into an equal volume of furfural $0.018M$ in I_2 was roughly three. However, it was noticed that yttrium was more extractable than strontium.

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