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SUBJECT: Chlorine Removal from the Darex Off-Gas

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ABSTRACT

A 2 M NaOH solution is a satisfactory scrubber for the Darex off-gas if sufficient nitrite is present to reduce all hypochlorite to chloride. If there is not enough nitrite produced in the scrubber solution by the reaction of nitrogen dioxide and nitrogen sesquioxide with sodium hydroxide, more reducing agent will have to be added. Both nitrite and sulfite rapidly reduce hypochlorite in basic solution. The scrubber solution can be used as long as it remains basic.

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1.0 INTRODUCTION

The present central off-gas system for the nuclear fuel reprocessing facilities is partially fabricated of stainless steel. To prevent excessive corrosion of this system all chlorine or volatile chlorine-containing compounds must be scrubbed from the Darex off-gas.

Chlorine removal is the major problem. While nitrosyl chloride (NOCl) is also volatile, it reacts rapidly with water to form chloride ion.¹ The reaction

has been used as a basis for a method of absorbing chlorine.^{2,3,4} The rate of chlorine absorption in ferrous chloride solutions is much slower than in sodium hydroxide.² Therefore, it was decided that a sodium hydroxide scrubber was preferable, despite the fact that the sodium hydroxide would be partially used up in reacting with oxides of nitrogen, which are also present in the Darex off-gas.⁵

The removal of chlorine by equation 1 would be satisfactory only if there were no chlorine vapor pressure above alkaline hypochlorite solutions and if it could be assumed that the alkaline waste would never be neutralized, thereby releasing chlorine through decomposition of hypochlorous acid. It was decided that the hypochlorite would have to be reduced to chloride before the scrubber solution could be discharged as waste. If the hypochlorite ion should demonstrate a chlorine decomposition pressure in basic solution, the reducing agent would have to be added before scrubbing. Sulfite ion offers a promising possibility for reducing alkaline hypochlorite to non volatile chloride. The nitrate ion, introduced by the reaction

and by the absorption of nitrogen sesquioxide,⁶ is also a possible reducing agent. Two molar sodium hydroxide was chosen as the maximum base concentration to be used, since it has been shown to provide the most rapid CO_2 scrubbing,⁷ and the sparingly soluble sulfite does not precipitate.

A simple method of analyzing the scrubber solution has not been developed. This problem may be simplified by a better knowledge of the relative concentrations of chlorine, nitrosyl chloride, and the oxides of nitrogen in the off-gas.

The competent, efficient work of the analytical laboratory, especially P. Thomason and W. Belew, made this study possible. The experimental work was performed capably by G. Woodall.

3.0 RESULTS

3.1 Chlorine Removal with 2 M NaOH

The hypochlorite ion is found to have a chlorine decomposition pressure in sodium hydroxide solution, since the hypochlorite concentration does not increase as rapidly as the chloride concentration when chlorine is bubbled into 2 M NaOH (Fig. 1). A reducing agent is needed to reduce the hypochlorite to chloride during scrubbing.

3.2 Use of Sulfite to Reduce Hypochlorite

Sulfite reduces all hypochlorite, produced when chlorine is bubbled into 2 M NaOH, to chloride, until all sulfite is completely used up (Fig. 2).

3.3 Effect of Nitrite and Nitrate on the Reaction Between Sulfite and Hypochlorite

The presence of nitrite and nitrate (introduced by equation 2) affects the reaction between sulfite and hypochlorite (Fig. 3). The steepness of the experimental curve indicates that nitrate is reacting with sulfite to produce nitrite and sulfate. The extension of the curve past the expected total reducing power of the sulfite before all sulfite is used up indicates that nitrite is reducing hypochlorite.

3.4 Use of Nitrite to Reduce Hypochlorite

Nitrite reduces hypochlorite to chloride in basic as well as acidic solutions (Fig. 4). The more gradual initial slopes are probably caused by the reaction of some impurity with hypochlorite, since samples taken in this region contained no hypochlorite.

Fig. 1. Chlorine Removal by the Reaction, $\text{Cl}_2 + 2\text{NaOH} \longrightarrow \text{NaCl} + \text{NaOCl} + \text{H}_2\text{O}$

Fig. 2. Chlorine Removal by the Reaction, $2 \text{ NaOH} + \text{Na}_2\text{SO}_3 + \text{Cl}_2 \longrightarrow 2 \text{ NaCl} + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$

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Fig. 3. Chlorine Removal in the Presence of Nitrite, Nitrate, and Sulfite

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Fig. 4. Chlorine Removal by the Reaction, $2 \text{ NaOH} + \text{NaNO}_2 + \text{Cl}_2 \longrightarrow 2 \text{ NaCl} + \text{NaNO}_3 + \text{H}_2\text{O}$

4.0 CONCLUSIONS

The question of whether or not sufficient nitrite is produced in a sodium hydroxide scrubber by reaction with the oxides of nitrogen evolved during the batch Darex fuel dissolution to reduce all hypochlorite produced in the scrubber during the chloride removal operation cannot be resolved until the compositions of the off-gas are determined. The presence of oxygen in the off-gas can also affect the nitrite concentration in the scrubber solution. Should sufficient nitrite be produced, only the alkalinity of the scrubbing solution needs to be followed during the scrubbing process, to make sure that the solution does not become neutralized. If the quantity of nitrite present is not sufficient, the reducing capacity of the scrubbing solution will also have to be followed and more reducing agent will have to be added as needed. Nitrite is the most satisfactory reducing agent because sodium nitrite is very soluble and because neutralization or acidification of the waste solution would introduce no new gas evolution problems. Sulfite can also reduce hypochlorite, but the sulfite apparently reacts with nitrate, and the sulphite would, if not completely exhausted, have a sulfur dioxide vapor pressure should the waste ever be neutralized or acidified.

The scrubber solution must be replenished before all base is used up, because, even though the hypochlorite can be reduced to chloride, in neutral or acidic solution chloride has appreciable vapor pressure and the reaction between chlorine and water is incomplete.

4.1 Experimental Procedure

The reagents used in each run (see Figs. 1-4) were dissolved in one liter of solution in a three liter flask immersed in a water bath at 23°C. The cooling water and reagent solutions were stirred rapidly and no temperature rise occurred due to the heat of reaction. Chlorine gas was passed into the solution at the rate of approximately 0.25 moles per hour. The chlorine bubbles were absorbed immediately upon entering the solution through a tube at the bottom of the flask. Duplicate 1-ml samples for each analysis were withdrawn periodically. As much as 47 ml of solution was removed in this manner, introducing a small error in the lattermost points on some figures, particularly Fig. 2. The pH change was determined by placing a drop of solution on pH paper after each withdrawal of samples. Chloride analyses were used as a means of following the reactions, and to prove the stoichiometry of the equations in Figs. 1, 2, and 4.

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