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Consolidated Fuel Reprocessing Program

IMPROVED PUREX SOLVENT SCRUBBING METHODS

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INTRODUCTION:

The Purex process uses about 30 vol % tri-n-butylphosphate (TBP) dissolved in a normal paraffin hydrocarbon diluent as a solvent to extract and separate uranium and plutonium from other components in spent reactor fuels. After extraction, scrubbing, and stripping operations, the solvent is treated to remove undesired impurities before recycling. The major impurities removed by conventional scrubbing with sodium carbonate are the TBP degradation products dibutylphosphoric acid and monobutylphosphoric acid. Sodium carbonate scrubbing is relatively successful; however, this process produces large quantities of permanent salts, does not remove the secondary complexants formed during degradation, and tends to form emulsions. The problem of permanent salts can be avoided by using scrubbing agents that can be decomposed into gases, or minimized by better utilization of sodium carbonate. Secondary complexants are thought to be formed by interactions of diluent degradation products with TBP or its degradation products. Diluent degradation products are also possible sources of emulsions in sodium carbonate scrubbers, through the formation of soaps by reactions with long-chain organic acids.

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This paper summarizes our studies of hydrazine and hydroxylamine salts as solvent scrubbing agents which can be decomposed into gases and reports on testing of countercurrent scrubbers and solid scrubber columns that produce lesser amounts of permanent salts. It also summarizes our studies of the acid-degradation of paraffin diluent and the options for removal of long-chain organic acids.

HYDRAZINE AND HYDROXYLAMINE SALTS:

The use of hydrazine carbonate in solvent scrubbing was developed and tested by German workers.¹ A process modification substituting oxalate for carbonate to eliminate gas formation and increase the complex stability was developed and described by Tallent et al.² Both scrubbing agents are at least as good as sodium carbonate for the removal of metal ions, dibutylphosphate (DBP), and monobutylphosphate (MBP); neither causes problems in the presence of long-chain organic acids, and the oxalate salt produces better phase separation. The disadvantages to their use are the toxic and suspected carcinogenic properties of hydrazine³ and the possibility of hydrazoic acid formation by the reaction of hydrazine with nitrous acid.⁴ While these problems do not appear to be insurmountable, they are reasons to examine other options.

The use of hydroxylamine salts for solvent scrubbing has been investigated, and they are capable of removing metal ions and DBP; however, they are significantly inferior to sodium carbonate. Tests in a system with three mixer-settlers showed that both scrubbing solutions gave good removal of U, Zr, DBP, and HNO_3 ; each had problems with interfacial crud formation. Most problems with hydroxylamine stem from the instability of the free base, which must be prepared from either the sulfate or the chloride. The scrubbing solution, which contains some free base, will oxidize slowly in air, especially at elevated temperatures.

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MINIMIZING SODIUM REQUIREMENTS:

One method for minimizing the use of sodium is countercurrent flow of the organic and the aqueous scrub solutions in a multi-scrubber system. This allows operation of the first scrubber until near exhaustion of the scrubbing solution, since the second scrubber acts as a backup to remove any material escaping from the first. No problems were observed in testing this concept in a three-unit mixer-settler system.

Another approach that reduces the use of sodium involves reacting sodium hydroxide with silica gel to form a layer of hydrous sodium silicate on the surface of the gel particles.⁵ This aqueous layer removes the reactable material from a contaminated solvent flowing through a packed column. In tests of this system, it was found that metal ions were very well removed by the packed column. The DBP was only partially removed, due

to distribution of NaDBP back into the organic phase; a water scrub would be required subsequent to the packed column to remove the NaDBP. The column packed with treated silica gel was found to be superior to sodium carbonate scrubbing in the removal of secondary complexants,⁶ probably because of the large number of theoretical stages in the column. The large amount of silica gel required may be a problem, but regeneration is possible, though complex. The use of the silica gel as a part of the feed to a glass-fixation process could reduce this concern. A major advantage of the packed-column method is the simplicity of the equipment required and the fact that the removed materials (including components that normally appear in interfacial crud) are retained on the surface of the silica gel.

DILUENT DEGRADATION AND ORGANIC ACID REMOVAL:

Degradation of saturated hydrocarbons in nitric acid is known to be catalyzed by NO_2 ,⁷ and this was confirmed to be the case in Purex systems.⁸ The degradation products included nitro alkanes, alcohols, nitro alcohols, alkenes, nitro alkenes, ketones, esters, and carboxylic acids. Fortunately, most of the compounds are probably innocuous in the operations of the Purex process; however, the esters and carboxylic acids have been implicated in the formation of secondary complexants.⁸ The most likely method for removal of long-chain organic acids is to first form the sodium salt by contact with a base (such as sodium carbonate) and then wash out the salt with water or very dilute sodium carbonate. The removal of esters would require hydrolysis followed by formation of the sodium salt and water scrubbing.

EMULSION FORMATION:

Mixer-settler tests showed that, while the presence of long-chain organic acids does increase the tendency toward emulsion formation with sodium carbonate scrubbers, the major problem is likely the formation of interfacial crud in the settlers when both zirconium and DBP are present in the solvent.

EVALUATION:

Based on the available information, if the reduction of permanent salts is desired, the use of one scrubber using a hydroxylamine-salt scrubbing solution followed by a sodium carbonate scrubber is indicated. This arrangement minimizes the amount of sodium carbonate makeup, since the hydroxylamine salt scrubber removes the bulk of the contaminants. The presence of the sodium carbonate scrubber improves the overall decontamination of the solvent and converts the long-chain organic acids to their sodium salts, allowing subsequent removal in a water or dilute sodium carbonate scrubber. If salts reduction is unnecessary, then scrubbing with sodium carbonate solutions alone should be used. In some specialized applications, the use of a packed solution of sodium-treated silica gel is advantageous.

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