Present and Future Roles of Solvent Extraction in Treatment of Nuclear Wastes

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Abstract: Solvent extraction has played a major role in development of the nuclear industry and has recovered much of the uranium from raw materials and essentially all of the plutonium and uranium from spent fuels. These operations produced a wide variety of radioactive wastes as well as the uranium and plutonium products. Solvent extraction worked well in the earlier nuclear facilities and should play a significant role in future cleanup operations.

INTRODUCTION

Solvent extraction has played a major role in the development of the nuclear industry, both nuclear power and the nuclear defense program. Practically all of the uranium ores were leached with acid, and the uranium was recovered by either solvent extraction or ion exchange. Other difficult chemical separations needed by the industry, such as removal of hafnium from zirconium, have been done largely with solvent extraction. Solvent extraction was used to separate the uranium and plutonium from the fission products and other components of the dissolved fuel from production reactors.

Solvent extraction processes were carried out on large scales and with very commendable success. However, substantially less need now exists for processing additional uranium ore, and the reprocessing of nuclear fuels in the United States has been stopped completely. A phase of the history of solvent extraction for these applications has come to an end. Advocates of nuclear power feel that there will eventually be a need for conserving fissile fuel and for fuel reprocessing, but clearly one phase of the nuclear industry in this country has been completed. Fuel processing continues in a few other countries, but the slow growth of nuclear power in the world, the stagnation of nuclear power in the United States, and the recent availability of fissile material from weapons programs do not make a revival of fuel reprocessing likely for the near future.

The principal interest now for separations in the nuclear industries is for waste and environmental problems, but solvent extraction is often not included in reference plans for treating radioactive wastes, despite the very good solvent
extraction research in recent years. Consider now some of the issues that may be preventing solvent extraction from receiving the attention for waste and environmental processing that it enjoyed in earlier stages of nuclear developments.

POSSIBLE FACTORS LIMITING THE INTEREST IN SOLVENT EXTRACTION

Differences exist in the separation needs for radioactive waste processing and the needs for recovery of uranium from ore or for reprocessing of spent fuel. There also have been important changes in environmental regulations during the decades since the establishment of the solvent extraction technologies used in what Alvin Weinberg called the "first nuclear era." Changes in attitudes that may hinder applications of solvent extraction processes for waste and environmental treatment have also occurred.

It seems strange to hear solvent extraction described as a "complex technology" at nuclear sites that once thrived on fuel processing and solvent extraction. Nevertheless, that attitude has arisen at some sites, and current plans often favor "universal" treatment methods that place essentially all of the wastes in final waste forms (usually glass), with few or no separation steps. When separations are required, ion-exchange systems may be favored because they appear to involve fewer steps. This could represent views that result from bad experiences with solvent extraction or views from a new generation of chemists and engineers who have less experience with the process. It appears to be an opinion of either new engineers or new management less familiar with those former successes.

Two modern issues do discourage application of either solvent extraction or, in some cases, any separation method. All separation treatments are discouraged when the material to be treated is inhomogeneous and difficult to characterize. Although it may be possible to reduce waste volumes by leaching contaminated sludges and other solids and concentrating the contaminants by solvent extraction, the costs of characterizing the inhomogeneous materials before and/or after treatment may far exceed the cost of preparing the entire material for disposal.

Even when the contaminated solids are homogeneous and easily characterized, there may be little justification for separations if the treated residue will be "assumed" to be contaminated simply because it came from a nuclear facility. Any separation process will be useful only if the decontamination can reduce the "level" of the solid waste sufficiently to lower its disposal cost.

Solvent extraction always leaves a trace of solvent in the aqueous raffinate because of solubility and entrainment. Under current regulations, only very low solvent concentrations can be allowed in discharged waters; therefore, additional treatment (perhaps carbon bed, oxidation, biodegradation) may be required.
OPPORTUNITIES FOR SOLVENT EXTRACTION IN RADIOACTIVE WASTE MANAGEMENT

Despite the difficulties faced in finding new uses for solvent extraction in treating radioactive wastes, several interesting and important developments have occurred, and some are likely to result in new applications. Several of these developments are described in other papers at this Topical Conference.

Removal of Actinides from High-Level Wastes

The bulk of the high-level radioactive waste stored in the United States is in alkaline precipitates, but one U.S. site and most foreign facilities appear to store the waste as acid solutions in corrosion-resistant stainless steel tanks. The volume of transuranium wastes from these materials can be reduced if the actinides (mostly transuranium) elements are concentrated. At the present time, none of the U.S. sites with alkaline wastes plan to dissolve the precipitates in their tanks to concentrate the actinide elements, but that operation remains an option. Horwitz and his associates [1] at Argonne National Laboratory have developed the TRUEX process, which utilizes synergistic extractants to remove actinides with high efficiencies. More recently, they have looked at combined extraction processes that can remove selected fission products (Horwitz et al. [2] and [3]) that also need to be removed. Interest in similar actinide removal processes exists in other countries. The DIAMEX process

under development in France (Madic et al. [4]) uses diamide extractants, and the POR process developed in Russia uses a phosphine oxide extractant (Brewer et al. [5]). Although the TRUEX process has received extensive study, there is greater interest in actinide separations in other countries, both for transmuting and for concentrating the actinides.

Removal of Fission Products

Selected fission products must be removed before any portion of high level waste (HLW) solutions can be treated as low-level waste (LLW), and significant efforts are being made to remove cesium from solution supernatant in the alkaline HLW tanks or from acid HLW. There is also a possible need to remove strontium and/or technetium from some of the wastes. Most of the U.S. work on removal of cesium involves the use of solid adsorbents or ion-exchange materials, not solvent extraction. However, the Czechs and Russians have developed a solvent extraction process using cobalt dicarbolide for removing cesium from acid solutions, like those in the HLW tanks at Idaho National Engineering Laboratory (INEL) as well as those in Russia (Brewer et al. [5]). They can modify the process to remove strontium as well as cesium. The Russians have applied the process on an engineering scale, but they used a diluent that would be difficult to use in the United States (nitrobenzene). They have recently reported that a different diluent can be used.

The French have reported a crown ether-based process for
cesium removal from acid solutions. Moyer and coworkers have been developing a crown ether-based solvent extraction process for removing technetium from alkaline solutions. Although there is significant interest in both of these processes, many people have significant concerns about the use of extractants as costly as crown ethers on this scale. This cost problem is being addressed.

**New Contactor Developments**

Developments in solvent extraction have not been limited to new reagents and processes; significant improvements have also occurred in solvent extraction contactors and in predicting the performance of contactors, especially for mixer-settler and centrifugal contactors. Improved contactor designs have come from several sites including the Oak Ridge National Laboratory and the Savannah River Technology Center, but the most extensive and complete studies have come from the Argonne National Laboratory (Leonard et al. [6], [7], and [8]).

Although there are no current applications of liquid membranes in nuclear waste treatment, extensive developments in these membranes during the past decade (in both supported membranes and microemulsions) may become important. These systems can be viewed as hybrids of solvent extraction and membrane technology. Notable features of liquid membranes are their ability to operate with very small inventories of solvent and the near elimination of entrainment. Both of these features make it practical to use more costly extractants, such as some crown ether extractants.

**SUMMARY AND CONCLUSIONS**

Solvent extraction research and development is alive and well in the nuclear fields, but the new needs are often in waste treatment rather than traditional separations. Some difficulties in applying solvent extraction result from technical performance, and research and development is needed to enhance those systems.

Other problems result from changes in regulations that have occurred since the days when solvent extraction dominated the nuclear process industry. Perhaps the most serious long-term problem for future applications of solvent extraction, or any separation process, is the lack of established levels of radioactivity that can be allowed in discharged solid wastes. Such limits are available for air and water, but similar regulations do not exist for complex solid mixtures, which always contain natural radioactivity as well as radioactivity that could have been added at the facility. No justification exists for removing radioactivity if the entire solid must be treated as radioactive regardless of its contamination. This is a difficult problem whose solution lies largely outside the capabilities of chemists and engineers working on solvent extraction.
Finally, problems seem to exist with the perception of the complexity and safety of solvent extraction processes. This perception exists within the technical community, and it should be possible and practical for those working on solvent extraction to correct the problem. It will not be sufficient to assume that facility designers and program managers will realize from raw data alone that solvent extraction is the approach to use. It may be necessary to address the "simplicity" of solvent extraction (a process that deals with liquids that can be easily pumped, a process that can operate continuously, and a process that can continuously remove degraded reagents). Solvent extraction will play major roles in nuclear waste treatment if good processes are developed and if the virtues of solvent extraction are presented effectively.

LITERATURE CITED


