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Why Have We Stopped Research on Liquid Centrifugal Separation

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Using high-temperature high-speed liquid centrifuges for lanthanides and actinides separation was originally proposed as a physical separation method in the Los Alamos ADTT/ATW concept [C. Bowman, "Liquid Centrifugation for Nuclear Waste Partitioning", LA-UR-92-1065 (1992)]. A small research group worked on establishing the feasibility of this approach from May 1994 to August 1995 [N. Li *et al*, "Solubility Separation under Centrifugation", LA-UR-95-1099 (1995) and "Decontamination of Nuclear Fuels with Centrifugal Separation", proceedings of Global 95 (1995)]. During this period, we investigated centrifugal separation in a concerted effort of experiments, theoretical analysis and numerical simulations. We discovered that owing to the ionic-composition-dependence of the sedimentation coefficients for the fission products and actinides, separation by grouping of molecular densities would not work in general in the molten salt environment. Alternatively the lanthanides and actinides could be transferred to a liquid metal carrier (e.g. bismuth) via reductive extraction and then separated by liquid centrifuges, but the material and technical challenges are severe. Meanwhile we have established that the reductive extraction procedure itself can be used for desired separations [L. M. Ferris *et al*, "Equilibrium Distribution of Actinide and Lanthanide Elements between Molten Fluoride Salts and Liquid Bismuth Solutions", *J. Inorg. Nucl. Chem.*, V.32, 2019(1970)]. Unlike conventional aqueous-based reprocessing technologies, reductive extraction separation uses only reagent (Li) that reconstitutes carrier salts ($\text{LiF}\cdot\text{BeF}_2$) and a processing medium (Bi) that can be continuously recycled and reused, with a nearly-pure fission products waste stream. The processing units are compact and reliable, and can be built at relatively low cost while maintaining high throughput [L. S. Chow *et al*, "Continuous Extraction of Molten

Chloride Salts with Liquid Cadmium Alloys”, proceedings of Global 93 (1993); N. Li *et al*, “Mixing of Molten Salt in Liquid Metal in a Turbulent Centrifugal Contactor”, LA-UR-95-4207 (1995)]. Therefore the research effort on developing liquid centrifuges for separations in ADTT/ATW was terminated in late 1995. This paper will discuss the various aspects involved in reaching this decision.

1 Sedimentation Coefficients

In ionic solutions, the sedimentation coefficients of solutes depend not only on their molecular densities but also on their valences. For a strong electrolyte in the dilute limit, the sedimentation coefficient s is determined by the following Svedberg relation:

$$\frac{s}{D} = \frac{M_s(1 - \rho_0/\rho_s)}{nRT}$$

where D is the mass diffusion coefficient, M_s is the molecular weight of the solute, ρ_0 and ρ_s are the densities of the solvent and solute, n is the dissociation number (for solute MF_m , $n = m + 1$), R is the gas constant and T is the absolute temperature of the solution. This dissociation number correction on the sedimentation coefficients prevented the grouping of the sedimentation by molecular densities. Table 1 of the sedimentation coefficients for various chloride salts measured in aqueous solutions illustrates this effect. For weak electrolytes the problem is more complicated and not well understood. In molten salts environment, it is known that some fluorides tend to form complexes which makes centrifugal separation very uncertain without extensive and costly experimental tests.

2 Material and Technical Barriers

Since centrifugal separation depends on the differences in sedimentation coefficients and the grouping of these coefficients for actinides and lanthanides are disrupted by the ionic effects in molten salts, transferring the solutes into a liquid metal carrier was considered. In their elemental forms, actinides and lanthanides can be separated via grouping of the densities. However, the liquid metal medium exacerbated the structural material problems for high-speed high-temperature liquid centrifuges.

Salt	c_0	D [10^{-5} cm ² /s]	$(s/D)_{exp}$ [10^{-9} s ² /cm ²]	$(s/D)_{Svedberg}$ [10^{-9} s ² /cm ²]	n	density (g/cm ³)
HAuCl ₄ †	0.0403	1.5±0.3	5.3±1.2	5.1	2	3.9
CuSO ₄	0.111	0.41±0.08	2.4±0.5	2.3	2	3.603
CsCl†	0.232	1.7±0.3	1.9±0.4	2.5	2	3.988
CsCl	0.086	1.9±0.4	2.5±0.5	2.5	2	
ErCl ₃	0.177	0.90±0.2	1.4±0.3	2.1	4	4.1
LaCl ₃	0.081	0.78±0.2	1.5±0.3	1.8	4	3.842
SrCl ₂	0.077	0.99±0.2	1.2±0.2	1.4	3	3.052
NaCl†	0.089	1.7±0.3	*	0.63	2	2.165

Table 1: Type of salt solution, c_0 , D (from experiment), (s/D) (from experiment), (s/D) (from Svedberg relation), and n for $\Omega = 35000$ rpm. * - not fully equilibrated. † - $\Omega = 25000$ rpm.

2.1 Material Strength Problems

The most difficult structural material problem is the degradation of tensile strength with increasing temperatures. First of all, for attaining reasonable separation ratio at sufficient rates, the centrifuges must be operated at very high speeds. Analyzing the forces on a thin ring of material rotating along its cylindrical axis, we obtain the maximum rotational speed (terminal velocity) allowed by the tensile strength σ of the material:

$$v_T = r\omega = \sqrt{\sigma/\rho}$$

where ρ is the material density. The terminal velocities for various high strength steels and alloys at room temperatures are in the range of 400 to 500 m/s. For certain carbon fiber/resin, this v_T can reach 700 m/s at room temperatures.

Two factors, however, greatly reduce the maximum rotation speeds for centrifuges. First, the tensile strength of materials decreases rapidly for temperature above a few hundred degrees centigrade (see for example, ASM Metal Handbook). For instance, the various groups of ultrahigh-strength steels (e.g. AISI/SAE 4130, 4110 and 4340 family) possess the highest tensile strength at room temperature, as high as 2000 MPa. With a density of 8.5 g/cm³, the terminal velocity v_T is about 485 m/s. At temperatures above 500 °C, the tensile strengths typically drops more than 30%, leading to a reduced v_T of about 433 m/s. Some specialty steels and superalloys have been developed for high temperature applications, e.g. turbine blades in aerospace industries. These include, for instance, molybdenum and tungsten high-speed steels, powder metallurgy (P/M)

tool steels, polycrystalline cast superalloys and directionally solidified and single-crystal superalloys. Their respective tensile strengths at the required operating temperatures above $500\text{ }^{\circ}\text{C}$ are typically only 800 MPa , or v_T of about 320 m/s . Some composite materials can have very high terminal velocity owing to their high strengths and low densities, but they can not be used above their formation temperatures, which is only a few hundred degrees centigrade. Our report in the Global 95 proceedings outlined the requirement for a liquid bismuth based centrifugal separation unit. It is clear that the requisite terminal velocity of the centrifuges is near the limit of the available materials even at room temperatures.

The second factor is the inclusion of the stress owing to the finite thickness of the centrifuge shells and the additional load from the liquid. For a cylindrical shell of finite thickness, the terminal velocity at the inner surface (used in calculating separation ratios and rates) is smaller than that of a thin ring. In addition, the rather wide gap of the centrifuge required for reasonable separation ratios (equivalent to small numbers of stages required for a certain separation goal) imposes significant load on the structures. For bismuth with a density of about 10 g/cm^3 , this load can be more than a few hundred MPa , a significant fraction of the structural material's tensile strength.

2.2 Technical Barriers

From the proceeding discussion one can conclude that building the liquid centrifuges for separating lanthanides and actinides at high temperatures would some radical technical innovations. First, the structural materials (esp. the outer centrifuge shell) have to be at much lower temperatures than the liquid medium temperature. This would require a very efficient cooling system.

Secondly, if a reasonably long operating life of the centrifuges is required, they cannot be operated in batch mode because of the stress cycles necessarily encountered. However, truly continuous flow operation of liquid centrifuges has not been attained in the centrifuge industry (the so-called continuous flow centrifuges perform loading and unloading at greatly reduced rotation speeds). Several ideas have been proposed but none has been tested. The development time and cost would be significant.

3 Conclusion

Building high-temperature and high-speed liquid centrifuges for separating lanthanides and actinides presents severe technical challenges. The foregoing discussion touched only upon the several main ingredients in this complex issue. Many other pertinent aspects were not mentioned or were unknown. The checkered history of a multibillion dollar R&D effort in U.S. to develop gas centrifuges for uranium enrichment testifies to the technical and engineering difficulties one might encounter. In the meantime, metallurgical processes for efficient separation of various groups of fission products and actinides have been found in molten salt reactor and fast breeder reactor experiments. Many experimental results strongly suggest that the desired separations can be achieved and some laboratory scale, or even engineering scale equipment for such processes have been successfully built and operated. There are certainly many problems in adopting these processes for the ADTT/ATW concept, but the changes are relatively a straightforward extrapolation of the working procedures, well within the existing material and technical capabilities. Given that better alternatives exist for lanthanides and actinides separation, we terminated our research on developing high-temperature high-speed liquid centrifuges. Some of the experience we obtained can be readily transferred into building efficient centrifugal contactors used in reductive extraction processes.