

Coleman C F, Brown K B, Moore J G & Crouse D J. Solvent extraction with alkyl amines. *Ind. Eng. Chem.* 50:1756-62, 1958.
[Oak Ridge National Laboratory, TN]

Empirical and fundamental studies are summarized that show how the chemistry of amine extraction parallels resinous anion exchange, with important differences that include the versatile control of extraction selectivity through choice of amine class, structure, concentration, diluent type, and aqueous medium. [The SC⁹ indicates that this paper has been cited in over 100 publications since 1958.]

C.F. Coleman
Chemical Development Section
Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

May 11, 1984

"Around 1950, the Oak Ridge National Laboratory Raw Materials Section under the leadership of K.B. Brown launched an intensive search for solvent-extraction reagents that could (in contrast to ether and TBP) extract uranium from sulfuric acid leach liquors.¹ This was accomplished with the liquid cation exchangers (HDEHP, etc.²) and a suite of liquid anion exchangers, high-molecular-weight alkyl amines. The resulting Dapex and Amex processes eventually dominated domestic uranium production, spread worldwide, and provided a basis for innovative processes in other fields.^{3,4} Concurrently, examination and comparison of an increasingly wide range of amines gave a working picture of the different yet interdependent effects of amine class, symmetry, size, and shape, together with the physicochemical variables that control the extractions.

"This work had reached a stage of early maturity at the time the second UN Geneva conference was organized, and so it was possible to present a highly informative paper at that conference.⁵ With helpful editorial advice from the staff of *Industrial and Engineering Chemistry*, that 'Geneva' paper was

reworked to become this publication.

"Out of several hundred organonitrogen compounds tested, favorable performance was almost entirely limited to simple amines, plus (especially for use at high pH) some quaternary ammonium compounds. The amines of suitable size and structure extract acids to form salts that remain in stable solution in organic diluents. The order of affinities shown in acid extraction by the free bases and in anion exchange by their salts is generally similar to that shown by anion-exchange resins. The principal variables controlling metal-ion extractions are those affecting the formation of suitable complexes, the concentrations of anions competing for the amine, and the nature of the amine and diluent chosen. The aqueous pH is often a variable of major importance, operating indirectly through the hydrolysis equilibria of the metal ion or of the complexing and competing anions.

"To a certain extent, the extraction reactions and the responses to the extraction variables are similar for all of these extractants. Within these general similarities, however, there are large differences in specific behavior. Many of the extractions vary systematically with amine class and also, in much the same way, with degree of alkyl branching, so that a highly branched secondary amine acts in many respects more like a straight-chain tertiary than like a straight-chain secondary. This is also strongly influenced by the nature of the diluent, and the amine-diluent combination rather than the amine alone should be considered as the effective extractant.

"As was emphasized in the paper itself, this information was the product of the concerted work of many people. I believe that it (as also its predecessor 'Geneva' paper) was and is frequently referenced because the information provides extensive and often still definitive entry into many aspects of amine extraction. I still go back to it as a starting point on a new problem that might be solvable by amine extraction."

1. Coleman C F & Leuze R E. Some milestone solvent extraction processes at the Oak Ridge National Laboratory. *J. Tenn. Acad. Sci.* 53:102-7, 1978.
2. Blake C A, Jr., Baes C F, Jr., Brown K B, Coleman C F & White J C. Solvent extraction of uranium and other metals by acidic and neutral organophosphorus compounds. *Peaceful uses of atomic energy. Volume 28. Basic chemistry in nuclear energy.* Geneva: United Nations, 1958. p. 289-98.
3. Coleman C F, Blake C A, Jr. & Brown K B. Analytical potential of separations by liquid ion exchange. *Talanta* 9:297-323, 1962. (Cited 55 times.)
4. Coleman C F. Amine extraction in reprocessing. (Stevenson C E, Mason E A & Gresky A T, eds.) *Progress in nuclear energy. Series III. Process chemistry.* Oxford, England: Pergamon, 1970. Vol. 4. p. 233-85.
5. Coleman C F, Brown K B, Moore J G & Allen K A. Amine salts as solvent extraction reagents for uranium and other metals. *Peaceful uses of atomic energy. Volume 28. Basic chemistry in nuclear energy.* Geneva: United Nations, 1958. p. 278-88.