A STUDY OF THE LIQUID-LIQUID EXTRACTION OF BERYLLIUM

With Special Attention Being Given to the System in Which Beryllium Is Separated from Aluminum by the Solvent Extraction of their Thiocyanates

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ABSTRACT

The imminent need for supplies of beryllium in greater quantity and purity than the currently used processes for the extraction of beryl can produce, and the existence of large deposits of low-grade, acid-leachable beryllium ores have led to a search for new methods for use in beryllium extractive metallurgy. A promising new process based on the selective solvent extraction of beryllium from aqueous solution is described here.

A consideration of the factors influencing the stability and extractabioity of metal complexes led to the conclusion that the best ligands for the separation of beryllium from other metal ions of inert gas configuration, such as aluminum, by solvent extraction would be easily polarizable monofunctional anions. The thiocyanate ion as its ammonium salt was particularly promising for metallurgical application.

A number of systems, including those using thiocyanate were examined to learn the extent and selectivity of the beryllium extraction given by them and the system using ammonium thiocyanate as the extracting agent and methyl isobutyl ketone as the solvent was selected for special study. The influence of thiocyanate concentration, pH, presence of "inert" salts, metal concentration,

and other factors, on the distribution of beryllium and other metals in this system was studied. The chemical species taking part in the extraction were identified by analysis, spectrophotometry, and the theoretical examination of the influence of various factors (e.g. pH) on the extent of beryllium or aluminum extraction. Data on ore leaching, reagent recovery, and the stripping of the extracts were also obtained, and a tentative flow scheme for the extraction of beryllium from acid leachable bertrandite ores was set up.

Extraction systems using thiocyanate with other solvents have been investigated, some of them extensively, in the same way that the system using methyl isobutyl ketone has. Some of them would no doubt give good separation of beryllium from other metals, but there seems to be no advantage in using them rather than the methyl isobutyl ketone system.

TABLE OF CONTENTS

Table of Contents continued,

TABLE OF SYMBOLS AND ABBREVIATIONS

Symbols:

D_X = Distribution coefficient of component X.

$= \frac{\text{concentration of X in all forms in organic phase}}{\text{concentration of X in all forms in aqueous phase}}$

q_X = Nernst Constant of species X.

$= \frac{\text{concentration of species X in organic phase}}{\text{concentration of species X in aqueous phase}}$

E_X, % ext. of X — Percent extraction of component X

$V/v = \frac{\text{Volume of organic phase}}{\text{Volume of aqueous phase}}$

$\epsilon_x = \frac{\text{Total amount of X in organic phase}}{\text{Total amount of X in aqueous phase}}$

$= (V/v)\, D_X$

ϕ_X = fraction of X left unextracted in aqueous (raffinate) phase.

$D'_X = 1/D_X$

$\epsilon'_X = 1/\epsilon_X$

ϕ'_X = fraction of X left unextracted in organic extract, i.e., in the wash stages

$\beta_{Y/X}$ = The separation factor of Y from X

$= D_Y/D_X$

q/r = The ionic potential of an ion, where q = charge of ion, and r = radius of ion.

K_{fx} = Formation constant of X

[ ] : square brackets: indicate concentration of species enclosed.

M = any metal

M^{+n} any metal ion of oxidation state +n

ABBREVIATIONS FOR SOLVENTS AND REAGENTS

MIK - Methyl isobutyl ketone

1-hex - 1-hexanol

2-oct - 2-octanol

isoam ac - Isoamyl acetate

EtOAc - Ethyl acetate

EtOEt - Diethyl ether

KFR - Karl Fisher Reagent

DEFINITIONS OF TERMS

Extracting Agent - The reagent which reacts with the chemical species to be extracted to form the chemical species which extracts.

Extracting Medium or Solvent - The organic solvent which extracts the extracting chemical species from the aqueous phase.

System or Extraction System - The aqueous phase, solvent, material to be extracted, extracting agent, and any other reagents added which have a desired effect on the extraction, such as salting out agents or sequestering agents. The term is sometimes used to mean a particular set of reagents and solvents, and sometimes to mean a group of related systems, such as those using a particular extracting agent but different solvents.

Other terms are defined, as they are used here, in the body of the text ("solvent extraction" on page 8 "chemical species" on page 12).

LIST OF TABLES

List of Tables continued,

List of Tables continued,

LIST OF FIGURES

List of Figures continued,

CHAPTER I

SCOPE AND PURPOSE OF PRESENT INVESTIGATION

The extractive metallurgy of beryllium at present is mainly the processing of beryl, and the two major processes which have been developed for the treatment of this mineral[1] both depend on lengthy batchwise operations with many disadvantages. Heat treatment of the ore is required in both, reagent consumption is high, most reagents are uncrecoverable, and some are moderately expensive (e.g. EDTA). Neither method produces beryllium oxide in a very pure state; in fact further purification is required before it is used in producing the metal[2]. The extension of these processes to other types of beryllium ore would probably not lead to economic production especially if the ore was one of those of lower grade which will have to be used in the future. It is unlikely that either process could be much improved, either as to cost or as to purity of product.

Such processes have sufficed in the past because, until recently, beryllium has been demanded neither in large quantity nor in great purity, and the high grade beryl available could more than supply the demand. Recently, however, beryllium has been finding an amazing number of uses in space and nuclear technology both as the metal and as the ceramic oxide[1,2,3,4,5]. It seems likely that the use of the element in these fields will continue to increase, for both as the metal and as the oxide it has properties which are in many respects unique, and if the problem of its brittleness is overcome, or if useful alloys of it with other light metals are found, it will probably become the metal of choice wherever lightness must be combined with strength.

These new uses not only increase the demand for beryllium, but, in many cases, call for a metal of purity far greater than either of the present large scale processes can supply.

Increased interest in the development of new processes for the extractive metallurgy of beryllium has resulting not only from the demands of these new uses, but also from the discovery of new types of mineralization extensive and rich enough to be of commercial interest and the imminent necessity of using lower grade ores for which the two current processes are unsuited. Beryl production at present is tied to the very low cost of labour in the regions where it is mined (e.g. the Congo) and to the occurrence of small rich deposits. Most of the world's beryl is not economically mineable because it occurs thinly distributed through a useless matrix and the cost of handling the huge quantities of rock in order to obtain the beryl crystals (either by hand "cobbing" or by the newly developed flotation method) is excessive.

Deposits of non-beryl beryllium ores are presently attracting attention in many parts of the world. Bertrandite is found in huge deposits in the Topaz Mountains of Utah; Chrysoberyl in the Mount Wheeler region of Nevada, and in Alaska. Although these ores have a lower beryllium content than does beryl, the overall deposits in which they occur contain more beryllium than do the overall beryl deposits. While the supply of beryl is definitely limited, the supply of these ores appears to be very extensive.

Thus the nature of these non-beryl ores promises to make them more easily mined and handled than is beryl. Some of them also promise to be more easily extractable, because unlike beryl, they are attacked by sulphuric acid at moderate heat. The availability of some bertrandite ores which are entirely acid leachable prompted the work to be described here.

Many new methods of extracting or purifying beryllium have made their appearance in the literature[6,7,8]. However they are characterised by great expense or no improvement in the purity of the product, and none have yet been shown to be feasible on a large scale.

The present investigation is one of a number undertaken at this laboratory to establish process data useful in meeting the demands described above[9,10,11]. It was intended to develop a process for the separation of beryllium from the other metals, especially aluminum, which co-exist in its ores, by a process of solvent extraction.

Solvent extraction is the term used for liquid-liquid extraction when a species, dissolved in an aqueous solution, is partitioned between that solution and an organic solvent. When used for production or quantitative analysis conditions are maintained such that essentially all of the species enters the organic phase, i.e., it is extracted.

Such a process would begin with the leaching of the ore which would give an aqueous solution containing the beryllium. If, in the leaching and subsequent treatment of the leach, some of the other metals could be left behind the process would be that much improved. Thus, in this study, it was necessary to give some attention to the leaching of ores with the aim of completely removing the beryllium from the ore with as little consumption of reagents and as little coincident leaching of other metals as possible. Chief attention had, however, to be given to finding a suitable solvent extraction system for the selective extraction of beryllium from the solutions obtained by leaching, and to finding the optimum conditions for its use.

Optimizing the process required a knowledge of the way in which the extent of extraction varies with different conditions, e.g., the solvent, pH of the aqueous phase, concentration of extracting agent, etc. This knowledge had to be available both for beryllium and for the other metals which might be in the leach. A brief survey