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Purification of Beryllium by Acetylacetone — EDTA Solvent Extraction: Procedure and Chemistry*

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A procedure, described previously, for the preparation of high purity beryllium hydroxide has been improved and demonstrated on a kilogram scale, and a systematic study of its chemistry has been carried out. The $Be(OH)_2 \cdot xH_2O$ starting material is dissolved in acetylacetone (HX) as BeX_2, scrubbed with aqueous EDTA to remove metallic impurities, stripped with nitric acid, and precipitated with ammonia. The dried $Be(OH)_2 \cdot 0.3\ H_2O$, a granular, free-flowing powder, was obtained in 85% yield. Detectable metallic impurities totalled <5 parts/10^6. The variation of BeX^+ and BeX_2 formation quotients with ionic strength as well as the variation of BeX_2 and HX distribution coefficients with both aqueous ionic strength and organic phase composition are summarized. Decontamination efficiencies for some 13 cations were estimated to be very high. Effective purification was demonstrated on a sample of $Be(OH)_2$ starting material which was contaminated with 1000 parts/10^6 parts BeO of Na^+, Mg^{2+}, B(III), Cu^{2+}, Al^{3+}, Fe^{3+} and Cr^{3+}.

A previous publication[1] in this Journal described the development of a solvent extraction procedure in which BeO of high purity was prepared by extraction of beryllium acetylacetonate (BeX_2) into carbon tetrachloride from an aqueous phase containing EDTA (ethylenediamine tetraacetic acid, a 'masking' or sequestering agent). The present communication sets forth in outline the procedure which was subsequently adopted in larger scale (500 g/batch) BeO preparations. It was modified from that previously described: 1) to improve the yield greatly and 2) to improve the physical properties of the product—$Be(OH)_2 \cdot 0.3\ H_2O$. The parameters necessary to adapt this procedure to a particular process are also summarized here. Further details are given elsewhere[2].

APPARATUS, REAGENTS, AND PROCEDURE

Three pieces of equipment were used: 1) a stirred container in which the starting material was dissolved and the resulting organic phase scrubbed and stripped; 2) a container for precipitation of $Be(OH)_2$ by gaseous ammonia at 75°C; 3) a filter unit for collecting, washing, and drying the product. Since the container materials are an obvious source of contamination, plastics (Teflon and polyethylene) were used exclusively.

The procedure used, in addition to being more detailed, includes two important modifications of the one described previously[1]: 1) the $Be(NO_3)_2$ strip solution is scrubbed with chloroform to remove dissolved acetylacetone (HX) (this avoids subsequent precipitation of BeX_2) and 2) the precipitation is done with gaseous ammonia (Suñer, Bamberger and Laguna[3]) which produces a granular, easily handled product. The quantities given below are based on the equivalent of 100 g BeO in the starting material; batches equivalent to 600 g BeO actually were processed.

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[1] R. E. MOORE, J. H. SHAFFER and H. F. McDUFFIE, *Nucl. Sci. Eng.*, 17(2), (1963).

[2] C. E. L. BAMBERGER, H. F. McDUFFIE, and C. F. BAES, Jr., "The Preparation of Pure Beryllium Oxide by Solvent Extraction With Acetylacetone in the Presence of Ethylenediamine Tetraacetic Acid; Procedure and Chemistry," (Nov. 1964), USAEC Report ORNL-3733.

[3] A. SUÑER, C. BAMBERGER and F. LAGUNA, "Precipitation of Beryllium Hydroxide with Inert Gas-Ammonia Mixtures," The Third Conf. Nucl. Reactor Chem., TID-7641 (1962) p. 248.

1) Wet $Be(OH)_2$ starting material was dissolved at room temperature in 110% of the stoichiometric amount of acetylacetone (≈ 0.92 liter) with enough carbon tetrachloride added to make a total volume of 1.83 liter.
2) After the small amount of water produced was removed, the organic phase was scrubbed twice for 30 min with its volume of water. This was followed by two 3 to 4 h scrubs with its volume of $(NH_4)_2H_2Y$ solution (6 g EDTA/liter adjusted to pH ≈ 5 with ammonia). If the iron content was high (organic phase initially red or brownish in color) a third $(NH_4)_2H_2Y$ scrub was used. The organic phase was finally scrubbed twice with water.
3) The purified beryllium was stripped from the organic phase with 4.8 *M* nitric acid (1.67 liter) and the strip solution then scrubbed repeatedly (≈ 6 times) with 300 ml batches of chloroform until the remaining HX in the aqueous phase was ≈ 0.01 *M*.
4) The aqueous $Be(NO_3)_2$-HNO_3 solution was filtered (analytical grade filter paper in a polyethylene funnel) into the precipitation vessel, water was added to adjust the volume to 6.67 liter, and EDTA was added to 0.01 *M*. The solution was heated to 75°C and ammonia passed until the first appearance of a precipitate (≈ 1.67 liter/min for 1.5 h). At this point enough HNO_3 was added to dissolve the precipitate and then a 1:3 mixture of ammonia and nitrogen gas was used to complete the precipitation in ≈ 2 h. The precipitate was digested for 8 h at 60°C, the slurry filtered and the cake washed with about eight times its volume of water. After drawing dust-free air through filter to remove a portion of the water, the cake was washed twice with its volume of acetone. The cake was dried overnight by drawing air through the filter. The yield was ≈ 85%.

Analytical procedures employed in this investigation are described elsewhere[2]. Briefly, the course of the purification process and the kinetics of BeX^+ decomposition were followed by spectrophotometric measurements in the ultraviolet region. The behavior of contaminant cations was followed mainly by radiochemical methods.

THE PRODUCT

The product was a granular, easily dried, free-flowing powder, having approximately the composition $Be(OH)_2 \cdot 0.3\ H_2O$. Ignition of the product, 4 kg of which was prepared in 85% yield in 1-kg batches in all-plastic bench-scale equipment, gave BeO in which the *total* of measurable metallic impurities was <5 parts/10^6. Analysis of the $Be(OH)_2$ starting material by the Brush Beryllium Company showed (in parts per million parts of BeO) Fe, 116; Cu, 40; Si, 32; Al, 17; Na, 12; B, 6; Li, 6; Ni, 4; and Pb, 4. Table I presents the analytical information obtained on the final product.

X-ray diffraction of the $Be(OH)_2 \cdot 0.3\ H_2O$ product (performed by R. E. Thoma and D. R. Sears of

TABLE I

Analysis of $Be(OH)_2$ Product

Elements	Parts 10^6 Parts of Beo
Found	
Si^a	16
Na^b	2
Al^c	1.5
Cl^c	1
Ga^c	1
Cu^c	0.1
Mn^c	0.02
Below Detectable Limits	
Au^c, Dy^c, Eu^c, In^c, Ir^c, Lu^c, Re^c, V^c	< 0.02
Pb^c, Sb^c, W^c	< 0.1
Br^c, Er^c, Hg^c, Ho^c, Sc^c, Tb^c, U^c	< 0.2
Ag^d, Au^c, Cd^c, Cs^c, Gd^c, Li^e, Mg^d, Mo^c, Os^c, Ru^c, Sr^c, Th^c, P^f	< 1
Ce^c, Co^c, Cr^c, La^c, Rh^c, Se^c, Tm^c	< 2
B^e, Ba^e, Fe^e, Ge^e, Hf^e, K^e, Nd^c, Ni^e, Sn^e, Ti^e	< 4
Ca^d, Pr^c, Pt^c, Te^c, Tl^e, Zr^e	<10
$Zr^{c,d}$	<20
Rb^e	<40

[a] Spectrographic analysis; O. Brisco and others, Analytical Laboratory, Y-12. Since Si is an element very common in any laboratory atmosphere, the determinations usually lack precision at very low concentrations because of contamination. Spectrographic analysis on the separate batches before blending, showed the following in separate analysis:

Batch	Parts of Si 10^6	Parts of BeO
1	14	18
2, 3	16	4
4	10	18
Average	14	11

[b] Neutron activation; W. Ross, Analytical Chemistry Division, ORNL. Sodium content high, partially because of contamination during analysis.

[c] Neutron activation; W. Ross, Analytical Chemistry Division, ORNL.

[d] Spectrographic analysis; J. Norris, Z. Combs, and others, Analytical Chemistry Division, ORNL.

[e] Spectrographic analysis; O. Brisco and others, Analytical Laboratory, Y-12.

[f] Analytical Chemistry Division, ORNL.

Reactor Chemistry Division, ORNL), as prepared or after vacuum drying for 18 h at 90 to 95°C, indicated the presence of the alpha form[4] of $Be(OH)_2$, with no BeO detected. Electron microscopic examination of the product (performed by T. E. Wilmarth and co-workers, Analytical Chemistry Division, ORNL) revealed it to be in the form of rosettes made up of polycrystalline sheets which extended 1 μm or more in two dimensions, but were only about 0.015 μm thick (150 Å). Upon exposure to the electron beam for a prolonged period, a sample was converted by the resultant heating to BeO. This material revealed the same platelet structure, but the sheets were stacked together.

EXTRACTION CHEMISTRY

With respect to the chemistry of the purification process, systematic study of the effect of changes in solution composition upon important extraction parameters provided a basis for the information summarized in Table II.

The various equilibrium quotients listed are defined by the reactions

$$Be^{2+}(aq) + HX(aq) \rightleftharpoons BeX^{+}(aq) + H^{+}(aq) \quad Q_1 \quad (1)$$

$$Be^{2+}(aq) + 2HX(aq) \rightleftharpoons BeX_2(aq) + 2H^{+}(aq) \quad Q_2 \quad (2)$$

$$BeX_2\,(aq) \rightleftharpoons BeX_2\,(org) \quad Q_{DB} \quad (3)$$

$$HX(aq) \rightleftharpoons HX(org) \quad Q_{DX}. \quad (4)$$

It was not necessary to consider beryllium hydrolysis products because their concentrations were estimated not to become significant compared to $[BeX^{+}]$ or $[BeX_2]$ in the aqueous phase with increasing pH.

Studies of the kinetics of the extraction of beryllium suggested that the various steps were essentially instantaneous (limited only by mass transfer), except those involving the formation and hydrolysis of BeX_2 in the aqueous phase. The reaction

$$BeX^{+} + H^{+} \rightarrow Be^{2+} + HX$$

was found to be the rate-controlling step in the hydrolysis of BeX_2, the rate expression being

$$-d[BeX^{+}]/dt = k[BeX^{+}][H^{+}]\,. \quad (5)$$

Figure 1 shows the effect of ionic strength upon the rate of the reaction; the effect is consistent

TABLE II

Variation of System Parameters with Solution Composition at 25°C

Parameter	Relation	Solution Composition	Source
Aqueous Phase			
BeX^{+} Formation Quotient, Q_1	$\log Q_1 = -0.94 - \frac{1.018\sqrt{I}}{1 + 1.3\sqrt{I}}$	0.1 - 2 *M* NaCl	fn a
BeX_2 Formation Quotient, Q_2	$\log Q_2 = -3.07 - \frac{1.018\sqrt{I}}{1 + 0.4\sqrt{I}}$	0.1 - 2 *M* NaCl	fn a
BeX_2 Distribution Quotient, Q_{DB}	$\log Q_{DB} = 1.81 + 0.35\ I$ $\log Q_{DB} = 1.81 + 0.1\ I$	0 - 4 *M* NaCl 0 - 4 *M* NH_4NO_3	fn a fn b
HX Distribution Quotient, Q_{DX}	$\log Q_{DX} = 0.53 + 0.16\ I$ $\log Q_{DX} = 0.53 - 0.13\ I$	0 - 1 *M* NaCl 0 - 1 *M* HNO_3	fn c fn b
BeX_2 Solubility	$\log [BeX_2]_a = -1.527 - 0.35\ I$	0 - 4 *M* NaCl	fn a
HX Solubility	$\log [HX]_a = 0.238 - 0.16\ I$	0 - 1 *M* NaCl	fn c
Carbon Tetrachloride Phase			
BeX_2 Distribution Quotient, Q_{DB}	$\log Q_{DB} = 1.81 + 0.04\ M$	$M = [HX]_0 + [BeX_2]_0 = 0$ to $2.8\ M$ $[BeX_2]/[HX] = 5$	fn b
HX Distribution Quotient, Q_{DX}	$\log Q_{DX} = 0.53 + 0.10\ M$	$M = [HX]_0 + [BeX_2]_0 = 0$ to $2.8\ M$ $[BeX_2]/[HX] = 5$	fn b
	$\log Q_{DX} = 0.53 + 0.12\,[HX]_0$	0 - 1 *M* HX	fn b

[a] Moore, Shaffer, McDuffie, Baes and Bamberger (Ref. 1).

[b] Present measurements.

[c] The variation of HX solubility with I is based on data of Steinbach (Ref. 7). Variation of Q_{DX} with I is assumed from that for the HX solubility.

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[4] R. FRICHE and H. HUMME, *Z. Anorg. Chemie*, **178**, 400 (1929).

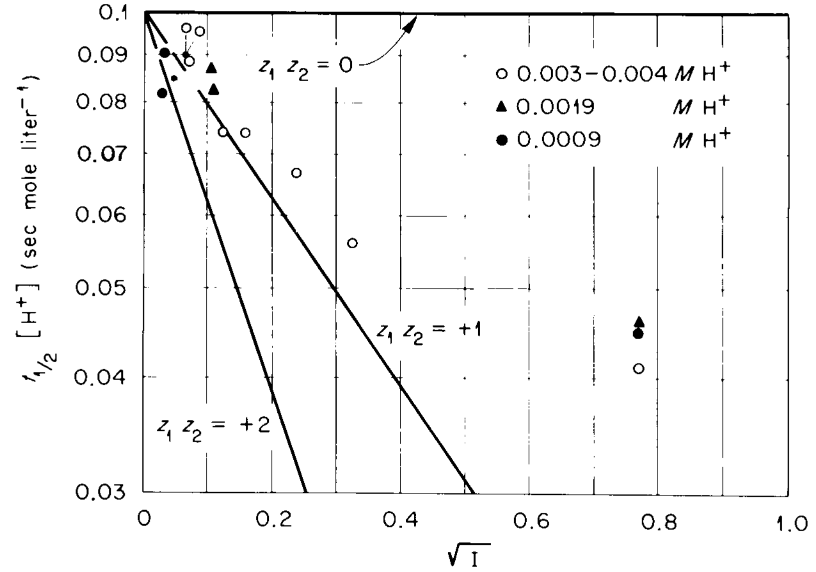

Fig. 1. The dependence of BeX_2 hydrolysis rate (half-time) on ionic strength and acidity. Solid curves indicate limiting slopes expected for reacting species of charge Z_1 and Z_2.

with the Brønsted[5] prediction for the reaction of two univalent, like-charged species to form an activated complex.

The decontamination of beryllium from a large number of metallic species is, of course, facilitated by the existence of the stable charged complexes which EDTA (H_4Y) forms in the aqueous phase with many cations

$$M^{z+}(aq) + Y^{4-}(aq) \rightleftharpoons MY^{(4-z)-}(aq). \qquad (6)$$

In the presence of both HX and EDTA, the extraction coefficient (D_M) of M^{z+} may be written in the form

$$D_M = \frac{[MX_z]_o}{([MY^{(4-z)-}] + [M^{z+}] + [MX^{(z-1)+}] \ldots [MX_z])_a}. \qquad (7)$$

The numerator is the concentration of the neutral metal acetylacetonate in the organic phase; it is assumed to be the only extractable species. The denominator, equal to the total aqueous concentration of the cation, contains a term for each species assumed to be present in the aqueous phase. (Hydrolysis products are neglected in Eq. (2), since it is expected that these concentrations will, in most instances, be low compared with those of $MY^{(4-z)-}$ or M-X species.)

A function, useful for estimating the extractability of a given cation into the organic phase, was defined as

$$f \equiv \frac{[MX_z]_a}{([MY^{(4-z)-}] + [M^{z+}] + [MX^{(z-1)+}] \ldots [MX_z])_a}, \qquad (8)$$

that is, the fraction of the total aqueous concentration of M^{z+} in the extractable form.

For a given cation, D_M is proportional to f

$$D_M = f[MX_z]_o / [MX_z]_a = f\,Q_{DM}\ . \qquad (9)$$

While distribution coefficients, Q_{DM}, of metal acetylacetonates in the present system were measured only for BeX_2 (85), UO_2X_2 (0.3), FeX_3 (110) and AlX_3 (7.8), other values in the literature[6-8] suggest that Q_{DM} is probably of the order of 100 or less for most cations. If this is true, then f values can provide an order of magnitude estimate of D_M in cases where Q_{DM} is not known. Calculations of f were made[2] for all cases in which sufficient formation-constant data are available. The results are plotted in Fig. 2 as log f vs pH for HX = 0.1 M and EDTA = 0.02 M, typical conditions in the present procedure. The unique position of beryllium is fully consistent with the success of the purification method.

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[5] S. GLASSTONE, *Textbook of Physical Chemistry*, p. 1092, Van Nostrand, New York, (1943).

[6] J. P. MacKAVENEY, "Use of Acetylacetone Extractions in Ferrous Analysis," (Thesis) NYO-6507 (1957) p. 38.

[7] J. F. STEINBACH, "Acetylacetone as an Analytical Extraction Agent," (Thesis) NYO-6347 (1953).

[8] A. KRISHEN, "A Systematic Study of Solvent Extraction with Acetylacetone." (Thesis) NYO-6497 (1957).

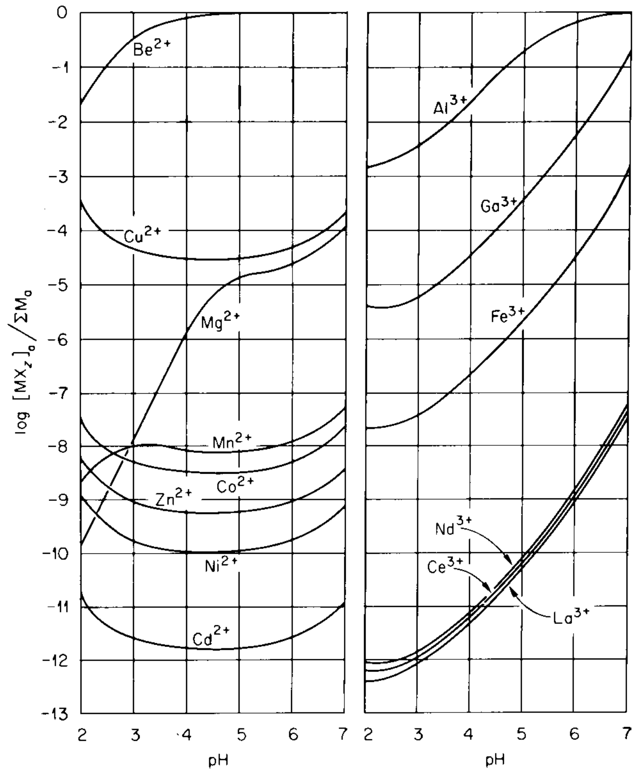

Fig. 2. The calculated fraction of aqueous cation concentration which is present as the extractable acetylacetonate (f in Eq. (8)), for various cations as a function of pH. 0.1 M aqueous HX, 0.02 M aqueous EDTA.

TABLE III

Purification of Contaminated $Be(OH)_2$
(1000 parts 10^6 parts BeO of Listed Impurities were Initially Present)

Step	Total Impurities Found (parts 10^6 parts BeO)[a]					
	B	Mg	Cu	Al	Fe	Cr
Initial Aq Phase after Be Extraction	990	986	260	363	66	1000
1st H_2O Scrub	10	5	117	30	13	--
2nd H_2O Scrub	--	--	144	15	17	--
1st EDTA Scrub	--	4	442	326	860	--
2nd EDTA Scrub	--	3	5	145	8	--
3rd EDTA Scrub	--	2	5	51	6	--
3rd H_2O Scrub	--	--	7	13	5	--
4th H_2O Scrub	--	--	4	10	7	--
Filtrate after Precipitation	--	--	16	47	18	--
Product	<4	<1	<4	<4	<4	<4

[a] These figures have been normalized to 1000 parts/10^6, the amount of impurity added initially, in order to correct for apparent systematic errors in spectrochemical analyses. The total parts 10^6 reported in each case was as follows: Mg, 775; Cu, 465; Al, 902; Fe, 989; Cr, 655.

The remarkably effective decontamination attainable by the purification procedure was demonstrated by processing a batch of $Be(OH)_2$ (equivalent to 23 g of BeO), to which soluble salts containing Na^+, Mg^{2+}, B(III), Cu^{2+}, Al^{3+}, Fe^{3+}, and Cr^{3+} were added (to 1000 parts/10^6 in each case) during the initial dissolution step. Analyses were performed at various stages in the procedure, giving the results shown in Table III. It is noteworthy that while Al^{3+} was not completely removed during the EDTA scrub steps, presumably because of low extraction rates, the remainder was retained in solution by EDTA during the precipitation step. To a lesser extent, Cu^{2+} and Fe^{3+} exhibited similar behavior; Na^+ and K^+ were found at all stages of the procedure, except in the product, the sum for Na^+ being many times the amount added initially. This may be attributed to the glass equipment used in this particular test. Silica was the only element consistently found in the product, two analyses giving 14 and 40 parts/10^6.

CONCLUSIONS

The purification method described is capable of good yield; 85% was demonstrated and over 90% should be possible on a larger scale. The method has a high tolerance for impurities, the reaction rates are high, the low temperature of operation simplifies the design of sufficiently noncontaminating equipment, and finally, the granular precipitate obtained is easily dried to a free-flowing powder by mild treatment (the voluminous precipitates of $Be(OH)_2 \cdot XH_2O$ otherwise often encountered require oven drying, with great risk of contamination).

Study of the chemistry of this system indicates that extraction of beryllium is adequately described by the assumed extraction equilibria and masking equilibria. The extraction coefficients for most impurities in the presence of EDTA are predicted to be very low from available stability-constant data; the behavior of those cations such as Al^{3+} and Fe^{3+} which have, in the past, been troublesome can be understood and, in most cases, dealt with in terms of their low reaction rates. The behavior observed for uranyl ion, for which the lowest decontamination factors (≈ 100) were found, should be examined further if this ion is present as a major impurity.

The procedure described can be varied with due consideration for the equilibria which appear to be involved. The organic phase used here is near the saturation limit for BeX_2 (2.5 M at 25°C). Lower concentrations can be used, though a slight decrease in Q_{DB} should result. While the amount of excess HX recommended (initially 0.4 M) is not especially critical, higher excesses should result in lower decontamination factors since D_M is expected to vary directly as $[HX]^z$. Lower values of [HX] will result in a lowering of the beryllium extraction coefficient, particularly at low pH values. A combination of a lower free HX concentration and a much higher $(NH_4)_2H_2Y$ concentration could be highly advantageous where very large amounts of impurities are present, since this would not only increase decontamination factors, but should also increase the beryllium distribution coefficient by the salting-out effect. The purity of the reagents used in the extractions and scrub steps is thought not to be especially critical in view of the high decontamination factors. The use of lower grades of carbon tetrachloride and acetylacetone should therefore be permissible. The purity of the nitric acid and the chloroform used during and after the back extraction steps, however, is thought to be much more important. Any impurities introduced here which can be precipitated by ammonia at 75°C in the presence of EDTA will enter the product. It should be possible to reuse the CCl_4-HX solution remaining after the beryllium back extraction; this contains essentially all the CCl_4 used and 60% of the HX. Another 20% of the HX could be recovered from the chloroform scrub solutions.

The solvent, CCl_4, was a fortunate choice in this procedure, since it has been found to result in a low distribution coefficient for UO_2^{2+} (0.3) and Al^{3+} (7.8)—two cations which, otherwise, might be more difficult to separate from beryllium. From data in the literature[7-9], it may be concluded that substitution of pure acetylacetone or acetylacetone in chloroform as the extractant would result in higher distribution coefficients and poorer removal for these, and perhaps other, cations.

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[9] MASAYUKI TABUSHI, "Solvent Extraction of Metal Acetylacetonates," *Bull. Inst. for Chem. Research, Kyoto Univ.* 37, (1959) p. 252.