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Characterizing and classifying uranium yellow cakes: A background

Hausen, Donald M

Uranium concentrates obtained from leach solutions, known as uranium yellow cakes, represent an intermediate step in the processing of uranium ores. Yellow cake concentrates are prepared by various metallurgical methods, depending on the types of ores. Samples of yellow cakes prepared under various methods were analyzed; examined in detail by means of x-ray diffraction, infrared spectra, and wet chemical methods; and classified by mineralogic methods. The cakes were classified as uranyl hydroxide hydrate, basic uranyl sulfate hydrate, sodium para-uranate, and uranyl peroxide hydrate. The experimental preparation methods and characterization methodology used are described, and the significance of structural types to the physical and chemical properties of yellow cake production, as well as the pyrolytic transformations at high temperatures, are discussed.

INTRODUCTION

Uranium production in the United States reached its peak in the late 1950s and early 1960s on the Colorado plateau, where prospectors with Geiger counters were found along almost every back road in most of the western states. Uranium was solubilized from all types of ores by a variety of processes, usually incorporating strong acid solutions (most commonly H₂SO₄), followed by precipitation as yellow cake concentrates. This represented the first stage of uranium recovery and concentration on the way to the production of enriched uranium that contained the required high percentages of the uranium isotope U-235, which fissioned easily and could sustain a chain reaction.

In a sense, alchemy played a major role in early yellow cake production. Initially, the compounds formed in yellow cakes were not identified; in 1970, the U.S. Bureau of Mines still referred to yellow cakes as the final precipitate formed in the milling process and considered it to be ammonium diuranate or sodium diuranate. The compositions were variable and depended upon precipitating conditions. Although several uranium compounds were identified and characterized in this period, none were reported. Mineralogic studies were pioneered through the integrated use of optical microscopy, x-ray diffraction (XRD), infrared spectra, differential thermal analysis (DTA), and chemical analyses.

Yellow cake concentrates were produced by Union Carbide Nuclear Corporation under various plant and laboratory conditions at several mill operations, including the now inoperative mills at Maybell, Rifle, and Uravan, Colorado, and Globe, Wyoming. Yellow-cake production continued intermittently at the UMETCO

operation near Blanding, Utah, until the late 1980s. Some production of uranium yellow cake concentrates still currently occurs in Wyoming.

The principal aims in this investigation were to identify the crystalline phases in uranium yellow cake concentrates and to investigate the various means to produce low-sulfate cakes by means of the mineralogical characterization of the stability ranges of uranium phases under varying conditions of pH and temperature. This study represented one of the early applications of process mineralogy to hydrometallurgical problems during the late 1950s and early 1960s.

URANIUM YELLOW CAKE COMPOSITIONS

The types of yellow cake are listed in Table I. Uranyl hydroxide hydrate is precipitated as a colloidal yellow cake from oxidized uranium liquors near neutral pH; it is usually difficult to filter. The major constituents of these low-sulfate cakes assay between about 80-85% UO_3 . Small amounts of sulfate (-1-3%) may be contained in the hydroxide phase as adsorbed sulfate ions or partly bonded sulfate. Variable amounts of ammonium (2-5%), alkalis, Na^+ , K^+ , and iron oxides are also retained. XRD patterns of this type of yellow cake are similar to the naturally occurring uranium trioxide hydrates described by Christ and Clark.⁴ This was confirmed by Hausen⁵ in yellow cake concentrates from the Uravan Mill in 1958.⁵⁶ Debets and Loopstra⁷ have since confirmed the similar structures of synthetic and natural uranium hydroxide hydrates.

Small amounts of ammonia are retained by surface adsorption or structural substitution in uranyl hydroxide hydrates. However, most (Hermans and Markesteyn⁸ and Deane⁹) favor the substitution of molecular ammonia for water in the hydrated uranyl hydroxide [$UO_2(OH)_2 \cdot xH_2O \cdot yNH_3$], resulting in ammoniates.

Basic uranyl sulfate hydrate near zippeite is formed in precipitates produced from oxidized uranium liquors near neutral pH. It is the major component of high-sulfate yellow cake, which is highly crystalline and easily filtered. Assays are between about 75-80% UO_3 . Sulfate content is high, ranging from about 6-10%. Small amounts of ammonia (2-5%) are also retained, along with minor alkalis and iron oxides. Zippeite was synthesized in 1952 by Frondell and Traill by adding ammonia to an aqueous solution of uranyl sulfate and allowing the mixture to stand.

Sodium para-uranate is precipitated at a relatively high pH (above 11) by sodium hydroxide. It was the predominant phase in yellow cake concentrates produced from the Rifle plant in Colorado in the early- to mid-1960s. X-ray patterns are close to those described by Wamser et al.¹⁰ No other crystalline phases were detected by XRD in the yellow cake concentrates from the Rifle plant. Para-uranate cakes assay between 81% and 84% uranium and contain virtually no sulfate. However, the sodium content is relatively high, near 10% Na_2O . Appreciable amounts of vanadium (34% V_2O_5) were also contained in cakes produced from the Rifle plant. The conversion of basic uranyl sulfates to para-uranates by caustic treatment at high pH was described by Hausen¹¹ in earlier XRD studies.

Uranyl peroxide hydrate, prepared only in the laboratory for experimental purposes, represents a potential yellow cake concentrate that has not yet been produced in operations. The compound was precipitated as a high-purity yellow cake from low pH uranium liquors by the addition of hydrogen peroxide. The uranium content of so-called peroxide yellow cakes may approach or exceed 90% UO_3 , with only traces of impurities. The composition and thermal decomposition of uranyl peroxide was previously described by Leininger et al.¹²

YELLOW CAKE PHASE CHARACTERIZATION

Relatively pure samples of each of the four major uranium phases have been characterized by XRD patterns, infrared spectra, and DTAs. XRD patterns (Figure 1) provide the most rapid means to identify the major phase(s) in most uranium yellow cake concentrates. Most samples of yellow cake from the Maybell, Globe, and Uravan mills contained mixtures of uranyl hydroxide and basic uranyl-sulfate phases. However, there are some similarities in XRD patterns between these two phases, suggesting possible isostructural lattices.

Infrared spectra (Figure 2) provide an additional means to distinguish and characterize each phase and evaluate the molecular bonding of uranium in yellow cakes. The molecular spectra of uranyl hydroxides and sulfates show strong absorption bands between 11.0 (μm) and 11.5 (μm), which are assigned to the antisymmetrical stretching frequency ν_3 of the uranyl group, according to Jones¹³ and Nakamoto.¹⁴ This band occurs near 11.5 (μm) for basic uranyl sulfate and near 11 (μm) for hydroxide. The molecular spectrum for the parauranate anion shows a much broader region of absorption, extending from 10.5 μm to 14.0 (μm).

DTAs of yellow cakes (Figure 3) also provide a means to distinguish and identify major uranium phases. In addition, DTAs are used to evaluate phase transformation (and removal of volatile impurities) during pyrolysis.

Uranyl Hydroxide Hydrate

DTA patterns of yellow cakes containing mostly uranyl hydroxide hydrate show four endotherms at 180(deg)C, 310(deg)C, 670(deg)C, and 820(deg)C and one exotherm at 420(deg)C. The first endotherm between 100(deg)C and 180(deg)C is attributed to the dehydration of both uranyl hydroxide and basic sulfate hydrates. A second endotherm near 310(deg)C is accompanied by the loss of structural water.

XRD patterns show a significant decrease in the crystallinity of the uranylhydroxide phase following the loss of structural water. A sharp exotherm at 420degC accompanies the recrystallization of anhydrous uranium trioxide (UO_3). Samples heated to 450degC show characteristic XRD patterns for UO_3 . At higher temperatures that are above 600degC, the UO_3 begins to lose oxygen in converting to U_3O_8 , accompanied by the third endotherm.

Changes in the 13-14 μm spectral region for UO_3 and U_3O_8 have been investigated by Hoekstra and Siegel.¹⁵ The decomposition of minor amounts of basic uranyl sulfates in samples also occurs in this temperature range and may contribute to the endothermic maximum near 660degC.

The final endotherm near 820degC is attributed to volatilization of sulfates, which occur in minor amounts as impurities. Corresponding infrared spectra confirm dehydroxylation near 230degC and the progressive destruction of uranyl groups above about 400degC. Absorptions in the 13 (μm) region correspond to uranium-oxygen linkages of the trioxide and uranate groups. De-oxygenation reaches a maximum intensity near 660degC and is accompanied by changes in the 13-14 spectral region for UO_3 and U_3O_8 .

Basic Uranyl Sulfate Hydrate

DTA patterns of yellow cakes containing basic uranyl sulfates show four endothermic reactions centering near 180degC, 330degC, and 860degC. The initial endotherm is attributed to dehydration, followed by dehydroxylation of the basic uranyl sulfate lattice at 330degC. XRD patterns show significant changes in the intensity and position of major reflections due to dehydroxylation. An endotherm near 670degC is attributed to the final breakdown of the uranyl sulfate phase. The final endotherm is attributed to vaporization of sulfates above about 800degC. Infrared spectra provide back-up characterization of phase transformations during pyrolysis.

Sodium Para-Uranate and Uranyl Peroxide Hydrate

DTA patterns of sodium para-uranate yellow cakes show relatively minor changes during pyrolysis to 1,000C. XRD patterns of the yellow cakes indicate a slight increase in calcine crystallinity, but no phase changes in the para-uranate phase.

DTA patterns of uranyl-peroxide hydrates also show four major endotherms and two exotherms. These include a dehydration endotherm between 100degC and 150degC, and the endothermic destruction of the uranyl-peroxide structure between 180degC and 220degC. A minor exotherm near 280degC is followed by a third endotherm at 300degC, where remaining excess oxygen is removed to form stoichiometric UO_3 . Samples heated to 300C are largely amorphous, but display incipient crystallinity of the UO_3 phase. A major exotherm between 360degC and 430degC is associated with the crystallization of the UO_3 phase, followed by endothermic de-oxygenation of UO_3 to U_3O_8 .

THE APPLICATION OF PYROLYSIS DATA TO PURITY SPECIFICATIONS

Calcination of yellow cakes at elevated temperatures serves essentially two purposes: to increase the uranium grade of the concentrate by the removal of volatiles and to remove certain impurities that may otherwise occur in deleterious amounts for further processing of uranium oxides. Water, ammonia, and sulfates are the major components that are removable during calcination. In the 1960s, the uranium grade of the concentrate had to exceed 75% U_3O_8 to meet AEC specifications.

Ammonia and water are removed at relatively low temperatures (

High-temperature calcination of yellow cakes usually causes a minor binding of uranium as complexes that are insoluble in nitric acid. Specifications require less than 0.1% insoluble U_3O_8 . For this reason, calcination temperatures should not be too high (less than about 700degC).

Hematite and maghemite are the major components of HNO_3 insols from most yellow cakes. Uranium probably forms insoluble complexes with iron oxides at elevated temperatures. In the 1960s, calcination temperatures were lowest at the Uravan mill, ranging between 450-500degC, resulting in higher amounts of residual uranyl sulfates. Temperatures at Maybell, Colorado, and Globe, Wyoming, mills were higher (600-700degC), resulting in a high conversion to U_3O_8 and lower remaining sulfates. The production of yellow cakes from the Rifle mill in Colorado contained essentially para-uranates that contained no sulfates.

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Donald M. Hausen is currently a consultant in process mineralogy in Salt Lake City, Utah.

For more information, contact D.M. Hausen, 1767 South Woodside Drive, Salt Lake City, Utah 84124; (801) 277-0883; fax (801) 277-0612; e-mail mjoanh@aol.com.

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