Hydrometallurgy 163 (2016) 130–136

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

The thermal decomposition of uranous sulfate hydrates

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ARTICLE INFO

Article history:
Received 30 June 2015
Received in revised form 29 March 2016
Accepted 30 March 2016
Available online 11 April 2016

Keywords:
Uranous sulfate
Thermal decomposition
Thermal analysis
TGA
Calcining

ABSTRACT

Uranous sulfate *x*-hydrate will thermally decompose into uranium oxide at high temperature, releasing SO_2 gas that can be recovered as sulfuric acid. The recovered acid can be recycled back to the prior hydrometallurgical crystallization step, thus offsetting the net acid consumption of the process while at the same time producing a more readily marketable oxide product. A thorough understanding of the thermal decomposition pathways of the various uranous sulfate *x*-hydrates is critical to the proper design of such a calcining process. The thermal decomposition pathways of uranous sulfate tetra-, hexa-, and octahydrate, including decomposition temperatures and intermediary products, were determined theoretically using thermodynamic data, and then verified experimentally using thermogravimetric analysis. All three hydrates were found to proceed through similar stages of decomposition: multi-step water loss, oxidation to uranyl sulfate, and finally decomposition to U_3O_8. These thermal events were observed to occur at markedly different temperatures for each of the hydrates, suggesting that differences in structural arrangement play a role in thermal stability. A decomposition mechanism is proposed based on theoretical and experimental data, and an explanation for the different behaviours of the three hydrates based on structural differences is postulated.

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1. Introduction

Uranous sulfate *x*-hydrate, $U(SO_4)_2.xH_2O$, will crystallize selectively from a supersaturated uranium(IV) sulfate solution, with the amount of water *x* depending mainly upon temperature. A hydrometallurgical process based on this phenomenon has been proposed previously Burns et al. (2016). One attractive aspect of this process is the ability to recover sulfuric acid from the precipitate by calcining, thus offsetting the acid required for crystallization, while at the same time producing a more readily marketable oxide product, as shown in Fig. 1. Little is known, however, about the thermal decomposition of uranous sulfate precipitates. In the present work, the thermal decomposition behaviour of crystalline uranous sulfate tetrahydrate, hexahydrate, and octahydrate is described.

2. Background information

It has long been recognized that the different uranous sulfate *x*-hydrates have distinct thermal decomposition fingerprints. Leroy and Tridot (1965) reported that $U(SO_4)_2\cdot 4H_2O$ dehydrates in two steps, with $U(SO_4)_2\cdot H_2O$ as an intermediary, followed by oxidation to UO_2SO_4, and finally decomposition to U_3O_8. Gil et al. (1979) reported on the thermal decomposition of ten different uranous-*M* sulfate *x*-hydrate double salts (with M = Cd, La, Li, Mg, Mn, Ni, V, and Zn), but not on pure uranous sulfate. Suzuki et al. (1990) used thermogravimetric analysis (TGA) to identify a tetrahydrate, a trihydrate, and a *n*-hydrate ($n \approx 1.7-2.1$), all of which decomposed to $U(SO_4)_2$ by 410 °C, but they did not study the process in depth. No data on the thermal decomposition of the hexahydrate or octahydrate have been reported.

Given the lack of published information on the compounds of interest, it is useful to review a closely-related compound, its oxidized analog, uranyl sulfate *x*-hydrate. The decomposition of $UO_2SO_4\cdot xH2O$ has been studied by a number of authors Notz and Jaffe (1963), Leroy et al. (1965), Cordfunke (1969), Cordfunke (1972), Sato et al. (1980). In each study, the authors used TGA and differential thermal analysis (DTA) to suggest a decomposition pathway for water loss. Notz and Jaffe (1963) observed three distinct endotherms during the decomposition of $UO_2SO_4\cdot 3H_2O$, which they attributed to the stepwise loss of single water molecules. (Leroy et al. 1965) found that two different decomposition pathways exist, starting with either the tetrahydrate or the hemiheptahydrate, each distinguished by different decomposition temperatures and intermediary x-ray diffraction (XRD) patterns. Cordfunke (1969), Cordfunke (1972) subsequently confirmed that there are two distinct decomposition pathways, but identified the 2.5-hydrate as the true form of the compound previously assumed to be 3-hydrate, and also identified several different phases of the monohydrate. Sato et al. (1980) found a stepwise pathway similar to Notz's, and found that the x-ray diffraction patterns for their 3- and 2.*x*-hydrates were the same, supporting Cordfunke's theory that

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http://dx.doi.org/10.1016/j.hydromet.2016.03.023
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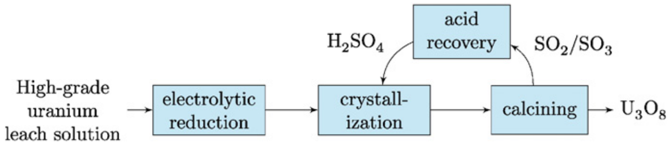

Fig. 1. Uranous sulfate crystallization process including calcining and acid recovery.

the 3-hydrate is simply a more-hydrated version of the 2.5-hydrate. In all, at least twelve crystallographically-unique phases of uranyl sulfate hydrate and anhydrate have been identified via thermal analysis.

The high-temperature thermal decomposition of both uranous and uranyl sulfate is more straightforward. Tridot (1966) reported that $U(SO_4)_2$ first oxidizes to UO_2SO_4, accompanied by the release of SO_2. Notz and Jaffe (1963) and Tridot (1966) both observed a sharp endothermic event centred at 755 °C which they attributed to a phase transition from αUO_2SO_4 to β UO_2SO_4. Upon heating in an oxidizing atmosphere to high temperature, all uranium oxides, and many other uranium compounds, ultimately decompose or convert to U_3O_8 Thein and Bereolos (2000). Uranyl sulfate is no exception, itself decomposing to U_3O_8 at high temperature.

The operating atmosphere during thermal decomposition has been shown to have an effect on the decomposition pathway and the stability of the intermediary products. Tridot (1966) observed that the onset temperature for the oxidation of $U(SO_4)_2$ was approximately 450 °C in a 10^{-2} mm Hg vacuum, 535 °C in dry oxygen, and 580 °C in SO_2. Under vacuum, the decomposition proceeded directly to U_3O_8, with only an inflection point in the TGA curve (as opposed to a plateau) to indicate the transitory presence of UO_2SO_4. Notz and Jaffé (1960) found that the atmosphere also affected the onset temperature for the final decomposition to U_3O_8:690 °C in helium, 750 °C in air, and 825 °C in a mixture of SO_2 and O_2.

3. Thermodynamic predictions

The stability of solid uranous sulfate hydrate under various conditions, as well as the decomposition products, can be predicted by thermodynamics. Chemical equations are written here in the following format:

$$A \xrightarrow{T_{eq}} B + C$$

where T_{eq} is the standard state equilibrium temperature (i.e., the activities of all reactants and products are 1). The equilibrium temperature for a given reaction can be calculated according to Eq. (1):

$$T_{eq} = \frac{\Delta H^\circ}{\Delta S^\circ - R \ln Q} \quad (1)$$

where ΔH° is the standard state enthalpy change for the reaction, ΔS° the standard state entropy change, R the universal gas constant, and Q the reaction quotient, which is the ratio of the activities of the product species divided by the activities of the reactant species, each raised to the power of its stoichiometric coefficient.

3.1. Water loss

The database of the chemical thermodynamics of uranium published by Guillaumont and Mompean (2003) contains data for only two uranous sulfate hydrates: the tetrahydrate and the octahydrate. Reactions for their complete dehydration can be written as follows (ΔG° in kJ mol $^{-1}$, T in K):

$$U(SO_4)_2 \cdot 4H_2O \xrightarrow{80^\circ C} U(SO_4)_2 + 4H_2O_{(g)} \quad \Delta G^\circ = 206.30 - 0.5763T \quad (2)$$

$$U(SO_4)_2 \cdot 8H_2O \xrightarrow{90^\circ C} U(SO_4)_2 + 8H_2O_{(g)} \quad \Delta G^\circ = 418.38 - 1.1527T. \quad (3)$$

From Eq. (1), this gives dehydration equilibrium temperatures of 85 °C and 90 °C for the tetra- and -octahydrate, respectively. The uncertainties in the published S° values for the two hydrates is around ±10%, however, making the calculated T_{eq} values only accurate to ±20 °C. In addition, if stable intermediary hydrates exist, as seems likely, the true transition temperatures would be different than calculated here.

3.2. Anhydrous uranous sulfate decomposition

Five possible decomposition reactions could play a part in the thermal decomposition of uranous sulfate, as follows (ΔG° in kJ mol^{-1}, T in K):

$$U(SO_4)_2 \xrightarrow{451^\circ C} UO_2SO_4 + SO_2 \quad \Delta G^\circ = 167.65 - 0.2314T \quad (4)$$

$$U(SO_4)_2 + \frac{1}{2}O_2 \xrightarrow{227^\circ C} UO_2SO_4 + SO_3 \quad \Delta G^\circ = 68.76 - 0.1374T \quad (5)$$

$$UO_2SO_4 \xrightarrow{889^\circ C} \frac{1}{3}U_3O_8 + SO_3 + \frac{1}{6}O_2 \quad \Delta G^\circ = 257.84 - 0.2219T \quad (6)$$

$$UO_2SO_4 \xrightarrow{916^\circ C} UO_3 + SO_3 \quad \Delta G^\circ = 225.64 - 0.1897T \quad (7)$$

$$UO_3 \xrightarrow{725^\circ C} \frac{1}{3}U_3O_8 + \frac{1}{6}O_2 \quad \Delta G^\circ = 32.20 - 0.0323T. \quad (8)$$

Given that the T°_{eq} value for Eq. (7) is higher than for both Eqs. (6) and (8), UO_3 should not form under standard state conditions. Only at the right combination of high pO_2 and low pSO_3 could UO_3 form, and even then only over a relatively narrow temperature range. It therefore seems unlikely that UO_3 plays a significant role in the thermal decomposition of uranous sulfate.

3.3. Phase diagram

Fig. 2 shows a phase diagram for the decomposition of uranous sulfate over the range 0–1000 °C, based on the solutions to Eqs. (4) to (8). The y-axis represents the partial pressure of either SO2 or SO3, depending on which gas is evolved during that stage of decomposition. The effect of oxygen partial pressure on the second decomposition step, Eq. (5), is shown with three pO_2 isobars. Also shown is the stability region of UO_3 at two different pO_2 isobars. U_3O_8 is the dominant phase at any oxygen partial pressure above 0.875 °C, demonstrating that it is always possible to convert $U(SO_4)_2$ into U_3O_8 as long as it is calcined at a high enough temperature.

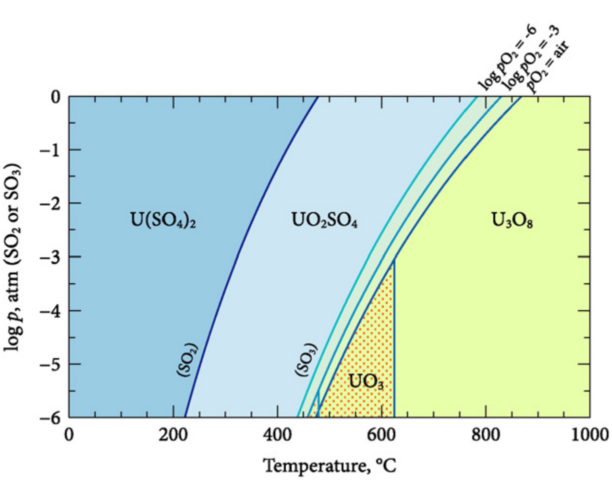

Fig. 2. Phase diagram of the U—S—O system for homogenous decomposition of $U(SO_4)_2$. pO_2 isobars are shown, along with their effect on the stability of UO_3.

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