



Uranous sulfate precipitation as a novel hydrometallurgical process for uranium purification



Alexander D. Burns*, Parisa Abbasi, David B. Dreisinger

The University of British Columbia, Department of Materials Engineering, Vancouver, BC, Canada

ARTICLE INFO

Article history:

Received 30 June 2015

Received in revised form 29 February 2016

Accepted 17 March 2016

Available online 23 March 2016

Keywords:

Hydrometallurgy

Uranous sulfate

Flow sheet

Demonstration

Uranous sulfate precipitation

ABSTRACT

Uranous sulfate is known to crystallize from uranium(IV) sulfate solutions upon the addition of sulfuric acid and the application of heat. This phenomenon, when coupled with a prior reduction process, could be exploited as a new way to selectively separate uranium from impurities in a high-grade leach solution. In the present work, the selectivity of uranous sulfate precipitation in the presence of the impurities Al, Cu, Fe, and Ni is demonstrated. A process employing this concept, including electrolytic reduction, precipitation, washing, drying, and calcining, has been tested on the bench scale from beginning to end, demonstrating that the process is technically viable.

© 2016 Elsevier B.V. All rights reserved.

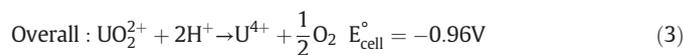
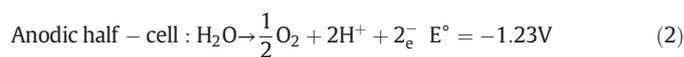
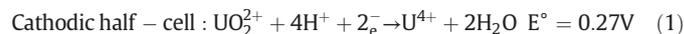
1. Introduction

Uranous sulfate is known to crystallize from uranium(IV) sulfate solutions upon the addition of sulfuric acid and the application of heat. This phenomenon, when coupled with a prior reduction process, could be exploited as a new way to selectively separate uranium from impurities in a leach solution, potentially complementing or replacing traditional solvent extraction and neutralization for high-grade leach solutions, or offering an alternative to ammonia or hydrogen peroxide precipitation. Prior work on the subject has generally focused on the fundamentals of electrochemistry, solubility, and solution chemistry, rather than its application as a hydrometallurgical process technology. In the present work, uranous sulfate precipitation is examined in the context of a process flow sheet. Results from a bench-scale test of the process are presented, including electrolysis, crystallization, and calcining, as well as a series of tests demonstrating the selectivity of the precipitation process in the presence of the impurities Al, Cu, Fe, and Ni, which are commonly found in Saskatchewan uranium ores.

2. Background information

2.1. Electrolytic reduction of uranium(VI) sulfate solutions

The electrolytic reduction of uranium(VI) in aqueous solution proceeds according to the half-cell reactions shown in Eqs. (1) to (3):



Past attempts at electrolytic reduction of uranyl solutions suffered from poor current efficiency and electrode fouling (Gurinov and Frolov, 1968). The use of ionomer membranes and modern electrode materials, however, could potentially overcome many of these issues. Researchers at the Power Corporation of Japan conducted a thorough study of this process, including polarization characteristics, aqueous speciation, diffusion characteristics, reduction rate, and current efficiency (Majima et al., 1986b; 1986a; Majima et al., 1987; Awakura et al., 1987). (Awakura et al., 1989) showed that the electrolytic reduction of uranium(VI) in sulfuric acid solutions can be carried out successfully in a simple two-compartment flow-through cell with a proton exchange membrane. After a certain fraction of the uranium was reduced,

* Corresponding author at: The University of British Columbia Department of Materials Engineering 6350 Stores Road Vancouver, BC V6T 1Z4 Canada.

E-mail addresses: alexander.burns@alumni.ubc.ca (A.D. Burns), parisa.abbasi@gmail.com (P. Abbasi), david.dreisinger@ubc.ca (D.B. Dreisinger).

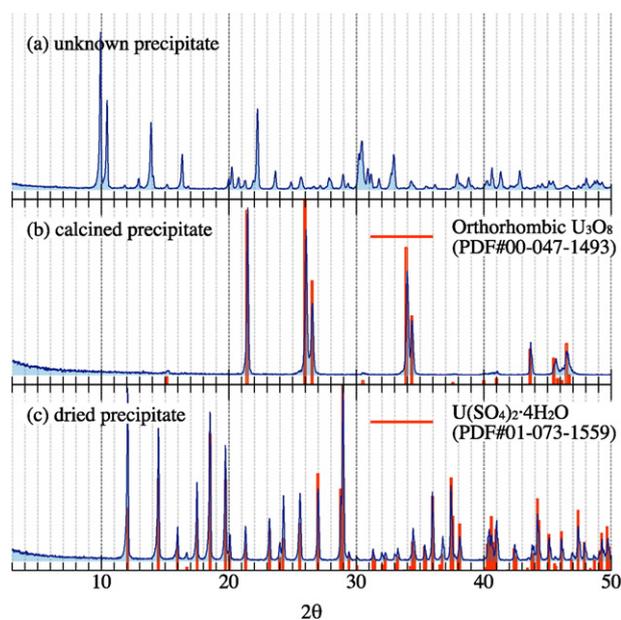


Fig. 1. XRD patterns of a: unknown solid precipitate; b: uranous sulfate tetrahydrate precipitate calcined in air at 800°C; c: dried uranous sulfate tetrahydrate precipitate.

the current efficiency, initially near 100%, declined markedly with the onset of hydrogen evolution. The overall current efficiency could be increased by improving the mass transfer characteristics in the cell, for example by increasing the flow-through rate, suggesting that hydrogen evolution is associated with diffusion limitations.

2.2. Precipitation of uranous sulfate

(Suzuki et al., 1990) studied the solubility of uranium(IV) in relation to temperature and sulfate concentration, showing that uranous sulfate is least soluble at high temperature and high sulfate concentration. They achieved a minimum solubility of approximately 15 g L⁻¹ uranium(IV) at 150 g L⁻¹ sulfate and 90°C, representing only 85% recovery when starting from a 100 g L⁻¹ synthetic leach solution. These highlights that, even under the best conditions, a substantial fraction of the uranium remains in solution, so it is important to start at as high a concentration as possible to achieve a reasonable recovery.

Uranous sulfate, U(SO₄)₂·nH₂O, can vary in its structure and amount of crystalline water *n*, depending on production conditions. (Giolitti and Bucci, 1905) and (Stabrovskii, 1979), in their studies of solubility, showed that the octahydrate (*n* = 8) is stable at temperatures below approximately 20°C, while the tetrahydrate (*n* = 4) is stable at temperatures above 20°C. (Suzuki et al., 1990) found that the precipitates at elevated temperatures consistently took the form of tetrahydrate, but at 25°C had a variable composition. Other structures have also been identified, including *n* = 6 (Burns et al., 2014), and *n* = of 5 and 9 (Schnaars and Wilson, 2012).

2.3. Process development

The electrolytic reduction and precipitation of uranous sulfate has never been practiced on an industrial or pilot scale. However, several similar processes for the production of UF₄ are known.

The Excer process was developed by American researchers at the Oak Ridge National Laboratory in 1956 as a cost-effective way to produce high-purity UF₄ (Higgins et al., 1958). The process involved ion exchange of a uranium-containing solution, stripping with HCl to create a high-purity uranyl chloride solution, the addition of a stoichiometric amount of hydrofluoric acid, and then electrolytic reduction and precipitation of UF₄. The feed solution could be sulfuric acid leach liquor,

Table 1

Aqueous-phase assays at the beginning and end of each test. Sulfate was adjusted to 2.0 mol L⁻¹ with sodium sulfate.

Test	Duration, h	Impurity <i>M</i>	Aqueous assay			
			[M] _{<i>i</i>}	[M] _{<i>f</i>}	[U] _{<i>i</i>}	[U] _{<i>f</i>}
1	72	–	–	–	169	70.0
2	72	–	–	–	145	46.3
3	72	Cu	14.9	15.2	167	73.3
4	72	Cu	30.2	30.0	152	56.4
5	72	Cu	68.2	69.0	156	99.4
6	72	Cu	138	135	156	156
7	72	Ni	15.8	16.1	136	140
8	72	Ni	32.1	33.5	144	105
9	72	Ni	78.1	79.7	160	97.5
10	72	Ni	164	167	196	166
11	72	Fe	15.0	15.7	140	61.8
12	72	Fe	31.2	31.8	137	76.5
13	72	Fe	64.5	65.9	134	115
14	72	Fe	132	134	128	128
15	72	Al	153	150	128	121
16	72	Al	17.1	16.0	139	75.5
17	240	Cu	127	126	120	87.0
18	240	Ni	142	139	132	72.7
19	240	Fe	113	108	132	71.9

sulfate, or chloride concentrate, or nitrate concentrate from solvent extraction. The electrolytic cell consisted of a mercury cathode, lead anode, and an Ionics CR-61 cation exchange membrane, and was operated at 80–90°C.

The SIMO process was developed by the French organization Société Ugine Kuhlmann for use in the Eurochem reprocessing plant in Mol, Belgium (Renaud, 1970). The process involved the dissolution of uranyl nitrate, followed by contact with sulfuric acid, removal of the nitric acid by distillation, electrolytic reduction, and finally the addition of hydrofluoric acid to precipitate UF₄. A variety of cathode materials were tested, including platinum and titanium, but a horizontal mercury cathode was chosen because of its resistance to HF and its ability to absorb contaminant cations. Platinum and iridium were used as anodes, and a polypropylene porous membrane separated the anodic and cathodic compartments of the cell. The pilot plant used three reduction cells in series to achieve 99% reduction. While the process seemed to be successful, a consistent problem was fouling of the mercury cathode by precipitated uranous sulfate. To prevent precipitation, the feed solution had to be diluted, resulting in a lower throughput.

The Spanish Atomic Energy Commission (SAEC) also developed an electrolytic sulfate-based process for the production of UF₄ (Duque et al., 1974). In addition to electrolysis, their study included details on fluorination, precipitation, filtering, and drying. A variety of electrode and cell body materials were tested for their ability to resist the

Table 2

XRD identity and chemical assays of the dried precipitates.

Test	XRD identity	Solids assay, wt.%					SO ₄ :U molar ratio
		U	SO ₄	Al	Cu	Fe	
1	Unknown	28.1%	47.8%	–	–	–	4.21
2 ^a	U(SO ₄) ₂ ·4H ₂ O	46.6%	37.7%	–	–	–	2.00
3	unknown	29.7%	53.0%	–	<0.01%	–	4.42
4	unknown	28.1%	51.5%	–	0.01%	–	4.54
9	unknown	27.5%	52.3%	–	–	<0.02%	4.71
11	unknown	25.9%	49.5%	–	–	<0.01%	4.74
15	NES	43.1%	NES	<0.15%	–	–	–
16	U(SO ₄) ₂ ·4H ₂ O	45.2%	38.7%	<0.19%	–	–	2.12
17	U(SO ₄) ₂ ·4H ₂ O	41.0%	38.0%	–	0.04%	–	2.30
18	U(SO ₄) ₂ ·4H ₂ O	46.7%	37.5%	–	–	<0.02%	1.99
19	U(SO ₄) ₂ ·4H ₂ O	43.2%	38.8%	–	–	0.06%	2.23

Samples 5, 6, 7, 8, 10, 12, 13, 14: Not enough solids for analysis.

^a A small amount of U(SO₄)₂·4H₂O powder was added as seed at the beginning of the test.

Download English Version:

<https://daneshyari.com/en/article/211854>

Download Persian Version:

<https://daneshyari.com/article/211854>

[Daneshyari.com](https://daneshyari.com)