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DISTILLATION MODELING FOR A URANIUM REFINING PROCESS

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OSTIAbstract

As part of the spent fuel treatment program at Argonne National Laboratory, a vacuum distillation process is being employed for the recovery of uranium following an electrorefining process. Distillation of a salt electrolyte, containing a eutectic mixture of lithium and potassium chlorides, from uranium is achieved by a simple batch operation and is termed "cathode processing". The incremental distillation of electrolyte salt will be modeled by an equilibrium expression and on a molecular basis since the operation is conducted under moderate vacuum conditions. As processing continues, the two models will be compared and analyzed for correlation with actual operating results. Possible factors that may contribute to aberrations from the models include impurities at the vapor-liquid boundary, distillate reflux, anomalous pressure gradients, and mass transport phenomena at the evaporating surface. Ultimately, the purpose of either process model is to enable the parametric optimization of the process.

Introduction

As a result of many years of operation as an irradiation and test facility, the Experimental Breeder Reactor II (EBR-II) has amassed a significant quantity of spent nuclear fuel. The spent fuel has been bonded with elemental sodium for ease of heat transfer from the fuel to the reactor coolant. Of the approximately 20 metric tons that make up the current inventory of spent fuel at Argonne, over 99% is uranium [1]. Treatment of the spent fuel is necessary to neutralize the reactive sodium and stabilize the uranium for storage and ultimate disposal.

The spent fuel treatment process includes both electrorefining and cathode processing to produce a stable uranium product [2]. Electrorefining is performed by loading sheared fuel elements into a molten LiCl-KCl electrolyte for dissolution and electrotransporting uranium as a cathode product. Fission products of the irradiated fuel are retained in the electrorefiner and placed into waste forms before final disposal [3]. Final refining of the uranium in the cathode product is achieved by distilling the process fluids, LiCl-KCl salt and cadmium, at the cathode processor. The cadmium, which resides below the molten salt phase in the electrorefiner, can serve as either an anode or cathode during the transport operation.

Equipment

Development of a distillation process for the purification of uranium can be traced to Argonne's original spent fuel processing effort [4, 5]. For this process, the uranium was intended to be recovered from a zinc-magnesium solution by a vacuum retort furnace. It is based on this initial research that the current design of the cathode processor has evolved.

Figure 1 shows a layout of the cathode processor equipment. The crucible assembly (splatter shield, process crucible, radiation shield, condenser assembly, and receiver crucible/support can) is bottom loaded into the cathode processor vessel by translating the assembly to below the vessel and raising the assembly until seated. For ease of operation, the cathode processor vessel is elevated above the operating floor. Horizontal motion of the crucible assembly is controlled by means of a trolley and rail assembly. With this configuration, the crucible assembly can be removed, dismantled, loaded or unloaded, and cleaned without disturbing the furnace components.

The furnace region of the cathode processor is heated by a passively cooled induction coil that susceptes to the graphite furnace liner which in turn heats the process crucible by radiation. The induction heating power supply is rated to 30 kW output at 2500 Hz, although only a 10-15 kW output is necessary to achieve the operating conditions. Isolation of the induction coils from the crucible assembly by a vacuum-tight confinement boundary prevents the migration of vapor species to the coils. A vacuum system, consisting of both roughing and diffusion pumps, can provide vacuums to as low as 0.01 Torr (absolute) in the cathode processor vessel. Also, an auxiliary heater in the upper region of the condenser, see Figure 1, assures that condensate is transferred down to the receiver crucible.

Following the loading of a process crucible with cathode product dendrites, the process crucible is placed on top of the crucible assembly and translated into the cathode processor vessel. Distillation of the salts and cadmium from the process crucible follows a downward mass transfer path to the receiver crucible. This downward flow minimizes the refluxing of condensate material as in conventional distillation columns. After completion of the run, the process and receiver crucibles are unloaded and ready for further processing.

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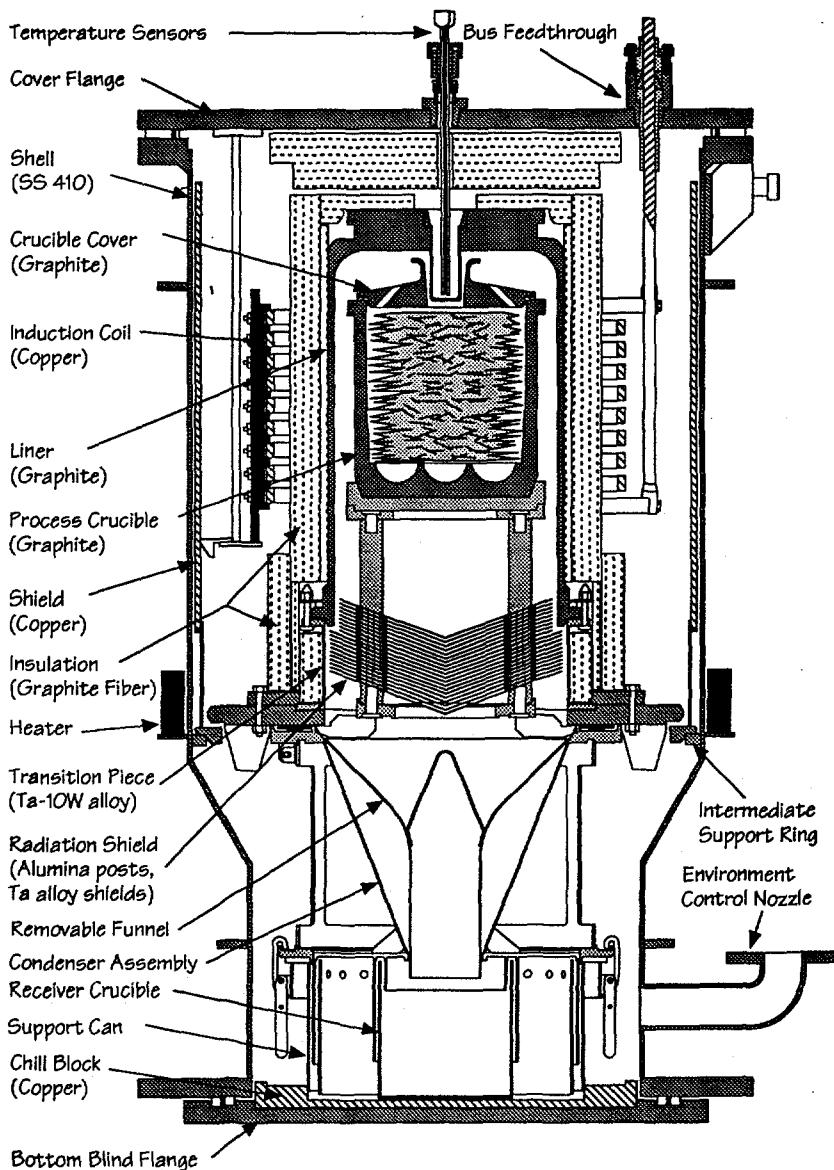


Figure 1. Schematic of Cathode Processor Equipment

The cathode processor is located in an atmosphere controlled, shielded hot cell of the Fuel Conditioning Facility (FCF) due to the activity of the spent fuel. Both oxygen and moisture contents are maintained at less than 100 ppm in the argon main cell of FCF. All operations in the hot cell, including those at the cathode processor, are performed remotely by overhead cranes, electromechanical manipulators, or mechanical (master-slave) manipulators.

Distillation Modeling

Since operation of the cathode processor is under moderate vacuums, on the order of 0.01 to 100 Torr, two principal methods may be applied to the distillation modeling. The first, equilibrium distillation, assumes that the vapor being evolved from a solution is in equilibrium with the residual liquid. One type of equilibrium distillation representative of batch operations is differential distillation where increments of vapor are removed from the liquid as fast as it is formed without appreciable refluxing [6-8]. The other method of distillation that may be applicable to the cathode processor operation is molecular distillation even though it is generally considered for high vacuum situations [7-11]. For molecular distillation, a non-equilibrant situation exists, that is, as the ebullition of vapor molecules from the surface of the distilland occurs they progress unobstructed towards condensation.

Equilibrium Model

The basis for the equilibrium model is the Rayleigh equation which accounts for the incremental displacement of material from the distilland to the gas phase. Equation (1) has been derived from the Rayleigh equation by integration and represents a mass balance of the vapor-liquid system,

$$N_{T_0} X_{i_0} = M_T Y_i + N_T X_i \quad (1)$$

where N_{T_0} is initial total moles of distilland,
 X_{i_0} is initial mole fraction of species i in distilland,
 M_T is total moles of gaseous species,
 Y_i is mole fraction of species i in gaseous phase,
 N_T is final total moles of remaining distilland,
 X_i is final mole fraction of species i in remaining distilland.

Other equations relevant to the equilibrium distillation model include the following molar balances and equilibrium relationships:

$$N_T = N_i + N_j + N_k + \dots \quad (2)$$

$$M_T = M_i + M_j + M_k + \dots \quad (3)$$

$$N_{T_0} = M_T + N_T \quad (4)$$

where N_i is final moles of species i in remaining distilland,
 N_j is final moles of species j in remaining distilland,
 N_k is final moles of species k in remaining distilland,
 M_i is moles of species i in gaseous phase,
 M_j is moles of species j in gaseous phase,
 M_k is moles of species k in gaseous phase,

$$P_i = X_i P_i^* \quad (5)$$

$$P_i = Y_i P_T \quad (6)$$

where P_i is vapor pressure of species i in gaseous phase,
 P_i^* is vapor pressure of pure species i ,
 P_T is total pressure.

Molecular Model

A rate of distillation or evaporation from the surface can be calculated using the Langmuir equation (7). By applying the kinetic theory of gases to an exposed surface, Langmuir derived this relationship to explain the nature of volatile molecules being evaporated.

$$w = P_i^* (M_i / 2 \pi R T)^{1/2} \quad (7)$$

where w is rate of evaporation from surface,
 M is molecular weight of species i ,
 R is gas constant,
 T is temperature.

Application of Models

For a two component system (A and B), equations (1) through (6) of the equilibrium model represent six equations and six unknowns (M_A , M_B , N_A , N_B , M_T , and N_T) after substitution of equations. For every component added to the system, another two equations are added. Solution of these simultaneous equations was performed by the geometric-arithmetic inequality algorithm [12]. The algorithm linearizes the non-linear equations so that the equations can be solved in logarithmic space. A spreadsheet macro was written for the solution of equations from the equilibrium model.

Equation (7) is dependent on time and distillation surface area since it represents a rate of distillation per unit area of evaporating surface. Thus, actual operating data (temperature and time) were input to the molecular model to determine incrementally the distillation of constituents. Since the area of the evaporating surface is a function of phase changes, density of constituents, and container geometry, these factors were included in the model. Also, since a multicomponent system was modeled, the mole fractions of components were considered. Again, a spreadsheet was used for the solution of the molecular model.

To date, two distillation experiments have been performed with the cathode processor. Both involved a dendritic cathode product containing depleted (<20% ^{235}U enrichment) uranium, LiCl-KCl eutectic salt, cadmium, and uranium trichloride. The second test also included some zirconium. Uranium trichloride is present in the salt as a result of the oxidation of the uranium metal by cadmium chloride at the electrorefiner. Small amounts of cadmium condense on the dendritic structure of the cathode product upon withdrawal from the electrorefiner. Hence, up to five components (U, LiCl-KCl, UCl_3 , Cd, and Zr) were modeled using both the equilibrium and molecular methods. Vapor pressures for the pure components were taken from the HSC thermochemical database [13].

Modeling Results

Modeling results as well as the actual results are given in Table I for the product from the cathode processor after distillation. Also

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Table I. Comparison of Modeled and Actual Results (Weight %)

Component	Test 1				Test 2			
	Initial	Molecular	Equilibrium	Actual	Initial	Molecular	Equilibrium	Actual
U	79.3	94.1	98.8	99.2	86.2	91.0	94.7	97.6
LiCl-KCl	18.0	4.7	1.0	0.0	11.1	6.6	3.2	1.0
UCl ₃	1.2	1.2	0.2	*	1.2	1.1	0.7	*
Cd	1.5	0.0	0.0	0.0	0.3	0.0	0.0	0.0
Zr	0.0	0.0	0.0	0.1	1.2	1.3	1.4	1.4

* Chlorine analysis not available so may be detected as U metal

included in Table I is the composition of the charge to the cathode processor for Tests 1 and 2. The charges were 3820 grams and 7018 grams, respectively.

The actual results for Test 1 are solely based on chemical analyses while those for Test 2 are based on both operational data and chemical analyses since not all of the analytical results are yet available. Samples for analysis were taken by remelting the cathode processor product and sampling the homogenized melt. The small amount of zirconium detected in the analytical samples for Test 1 can be attributed to a zirconia crucible coating.

If the distillation of LiCl-KCl and UCl₃ were increased in the equilibrium model, the actual values for both tests would compare quite favorably with the equilibrium model. Contrary to the equilibrium model, the molecular model shows a significant deviation from the actual results for both tests.

Discussion/Conclusions

A major assumption in both models is that of ideality, that is, the activity coefficients are assumed to be unity. For the molecular model, the activity coefficient of the salt in uranium is most likely greater than unity considering their solubilities. Thus, if an activity coefficient of greater than unity is used, the rate of salt distillation would increase and bring the modeled values closer to the actual. For the equilibrium model, the same effect would occur if the activity coefficient were greater than unity.

Looking at it differently, the models may not totally be in error. The actual values may be inaccurate because of systematic or random errors during the analytical and operational procedures. Or, as a compromise, both values may be in error due to side reactions within the melt which are not accounted for by the models.

Since the salt values for both models are always higher than the actual, the occurrence of a restrictive impurity layer or significant refluxing does not seem plausible to explain modeled and actual discrepancies.

Modeling of the cathode processor distillation should allow for adjustments to operating parameters for the optimization of the process. For example, by using the equilibrium model, both the total pressure and maximum temperature can be varied to indicate likely uranium recoveries, see Figure 2. A nominal 8 kg cathode product (15% salt and 1% Cd) was input to the model. From the plot, operation of the cathode processor would seem most

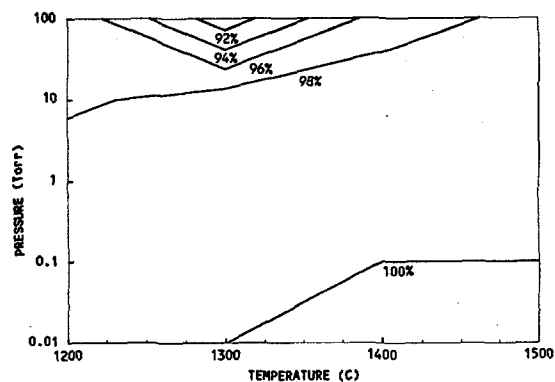


Figure 2. Uranium Recovery as a Function of P and T

effective at high temperatures (>1300°C) and low pressures (<0.1 Torr).

Distillation of a salt electrolyte (containing both eutectic LiCl-KCl and UCl₃), cadmium, zirconium, and uranium during cathode processing has been modeled by two different techniques; equilibrium and molecular. Although both techniques adequately modeled the distillation process, the equilibrium model presents the most potential for continued development.

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