*Thermodynamic Modeling of Hydrogen
Fluoride Production Relevant to Actinide
Residue Treatment*

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THERMODYNAMIC MODELING OF HYDROGEN FLUORIDE PRODUCTION RELEVANT TO ACTINIDE RESIDUE TREATMENT

by

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ABSTRACT

This report addresses issues specific to the generation of hydrogen fluoride via reaction of calcium fluoride with sulfuric acid. This process has been established on a commercial scale and is under consideration for treatment of calcium fluoride residues from uranium processing. Magnesium fluoride slags are also available as a product of uranium processing. The technique of using sulfuric acid for the production of hydrogen fluoride from magnesium fluoride is also under consideration as a residue processing scheme. In the current study, thermodynamic modeling was used to investigate these chemical processing systems. The results presented herein reveal information relevant to the selection of processing temperatures and conditions. Details include predicted effects in system composition based on operating temperatures for both the calcium fluoride and the magnesium fluoride systems.

I. INTRODUCTION

Fluor-Daniel Incorporated (FDI) is the primary site contractor for the environmental remediation management contract (ERMC) at Fernald, Ohio. As part of the environmental remediation effort, FDI has expressed an interest in recovering hydrogen fluoride (HF) for industrial use from calcium fluoride (CaF_2) and magnesium fluoride (MgF_2) uranium reduction slags. These slag inventories are present at Fernald and other uranium metal production sites. Currently, hydrogen fluoride is produced industrially by a two-stage reaction of fluorspar (calcium fluoride) with sulfuric acid (H_2SO_4).^{1,2} However, the recovery of HF from MgF_2 has not been demonstrated on an industrial scale. In an effort to facilitate laboratory scale and pilot plant scale studies of these reactions, Los Alamos National Laboratory (LANL) is modeling the thermodynamics of the processes under a number of experimental conditions. A brief description of the modeling approach is presented in the following paragraph. The results are discussed in the subsequent text.

In this work, computer modeling has been used to predict the equilibrium composition and product yield as a function of temperature for the reactions of interest. Los Alamos National Laboratory currently possesses very extensive and sophisticated capabilities in thermodynamic computer modeling. This modeling technique has been previously used in the evaluation of proposed variations in chemical processing conditions, such as changes in reactant compositions, system pressure, etc., in support of diverse chemical processing operations. The model

has been verified in several experimental works.^{3,4,5} The model involves rigorous computer calculations to generate predicted equilibrium compositions and phase assemblages for complex, heterogeneous chemical systems. The modeling operation is based on the thermodynamic principle that equilibrium (final) compositions correspond to the global free energy minimum for the specified chemical system. This involves the solution of large matrices of Gibbs energy expressions and requires substantial computer processing time. The models are designed to utilize advanced, computer-based numerical techniques.

II. PRELIMINARY RESULTS OF COMPUTER MODELING

Computer modeling was conducted separately on the MgF_2 and CaF_2 reactions with H_2SO_4 for the production of HF. The speciation as a function of temperature and reaction atmosphere (initial gas phase composition) were conducted. Initial results are presented herein.

A. Computer Modeling of HF Generation via the CaF_2 - H_2SO_4 Reaction in Air

As mentioned above, the production of HF from the reaction between CaF_2 and H_2SO_4 involves two stages. The temperature range over which the modeling was conducted bracketed the operating temperatures of both the 'Ko-Kneader' (reactor) and rotary kiln unit processes. The optimum temperature for HF formation is revealed in the modeling results (see Fig. 1). Note that an optimum temperature near 400°F was predicted by the computer model. This is close to the rotary kiln temperature used for the second stage of CaF_2 processing.² It is important to note that the optimum range is broad; only small variations in composition occur on either side of the optimum temperature (observe ordinate in Fig. 1). The optimum temperature can be more closely defined in further modeling efforts.

The model generated a set of predicted system compositions at each temperature (5 values) surveyed in the study. This involved the simultaneous solution of 81 Gibbs energy expressions for the formation of all possible substances in the chemical system. The results are reflected in the construction of the plot in Fig. 1. Further details are available upon request.

Fig. 1. HF generation as a function of reaction temperature for CaF₂ processing.

B. Computer Modeling of HF Generation via the MgF₂-H₂SO₄ Reaction in Air

The temperature range over which the modeling was conducted bracketed the operating temperatures (7 values) of both the 'Ko-Kneader' and rotary kiln as used in the CaF₂ processing operation. (Note: this temperature selection was based on information presented in the literature.^{2,6} As previously mentioned, no industrial scale demonstration has been conducted with MgF₂ directly.) The production of HF as a function of temperature is displayed in Fig. 2. Note that the mole numbers of MgF₂ are coplotted along with those of MgSO₄, an ancillary reaction product. An optimum processing temperature of ~660°F has been predicted for the generation of HF from MgF₂.

It is important to note that this optimum temperature *does not* coincide with the maximum depletion of MgF₂. In addition, the interactive dependence between HF formation and appearance of MgSO₄ has been revealed. The character of this interaction is not obvious. It involves complex chemistry and the variance of mole numbers for a suite of other ancillary species. (Note: the formation reactions for 91 substances were considered in this model.) Further details are available upon request.

Previous thermogravimetric studies were conducted to characterize the extent of MgF₂-H₂SO₄ reactions as a function of temperature. Based upon results of

those studies⁶, the evolution of HF from MgF_2 (27-mg scale) is complete by about 275°C.

Fig. 2. Partial compositional profile for MgF_2 reaction with H_2SO_4 and concurrent HF formation.

The present modeling effort predicted that the most efficient conversions are achieved at temperatures around 350°C or 662°F (see Fig. 2). Modeling smaller temperature increments around 662°F would specify the predicted optimum more closely.

The decomposition of unreacted H_2SO_4 to water vapor and sulphur trioxide gas ($\text{SO}_3(\text{g})$) is reflected in changes to the system composition. Fig. 3 shows the increase in mole numbers for water vapor and SO_3 . At the highest temperature studied, the moles of water and SO_3 are almost identical in magnitude. These features are shown coplotted with HF content.

The predicted formation of $\text{FSO}_3\text{H}(\text{g})$ (fluosulfonic acid or fluorosulfuric acid) is optimum at approximately 500°F (see Fig. 4). Fig. 4 also indicates that above this temperature, FSO_3H decomposes. The decomposition of FSO_3H explains the separation between the optimum temperature for HF formation and the minimum MgF_2 composition. The effects of H_2SO_4 purity were previously reported.¹ According to the results of that work, use of H_2SO_4 of greater than

99% purity was not advised. The $\text{SO}_3(\text{g})$ evolves from the H_2SO_4 decomposition and forms FSO_3H in a gas phase reaction with HF . For the $\text{MgF}_2\text{-H}_2\text{SO}_4$ reaction, operational temperatures should be selected to obviate the formation of FSO_3H .

Traditionally, these processing schemes are conducted in air. We investigated the effects of a nitrogen atmosphere over the chemical system. The model revealed that the speciation and optimum yield temperatures were not significantly affected when the atmosphere was changed from air to N_2 .

Fig. 3. Effect of H_2SO_4 composition on the appearance of selected species.

Fig. 4. Plot showing the relationship between MgF₂, HF and FHSO₃ mole numbers as a function of temperature.

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