Simulation and optimization of drying and salt formation process for radioactive high-salt waste liquid of medical isotope test reactor

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Abstract. Medical isotope test reactor is the first reactor in the world. In order to implement the principle of minimizing radioactive waste, the radioactive waste liquid adopts advanced drying and salt formation technology. According to the current dry salt formation technology a number of problems arise due to the complexity of the feedstock waste stream. In this study, a thermodynamic electrolyte simulation model was developed and its predictive accuracy was verified for complex electrolyte systems. Then, sensitivity analysis and discussion of the operating parameters such as temperature, pH and salt adjustment of the dry salting technology are presented. The new approach of the thermodynamic electrolyte simulation model has been used to improve and optimise the safety aspects of the technology and the associated process configuration. It provides a certain general idea and follow-up theoretical guidance for drying salt formation technology.

1 Introduction

Environmental issues in the nuclear industry have always been a major concern[1]. Compared to cement curing technology, the dry salt technology has the advantages of good capacity reduction, low overall costs and high automation[2]. At present, many research institutions at home and abroad are carrying out independent research and development. However, researchers are well aware that there are obvious limitations in the current research on this technology. Although several companies have achieved good results in modelling a variety of radioactive wastes and sludges [3,4]. Subsequently, several research institutes and enterprises in China have carried out research work on drying into salt technology[5-10]. With the rapid development of the nuclear industry, the sources of high-salt waste fluids have increased. The more representative ones include those from isotope extraction, nuclear fuel reprocessing and decommissioning of nuclear facilities. In particular, the medical isotope test reactor is the first reactor in the world. In order to better realize the principle of minimizing radioactive waste, the radioactive waste liquid is dried and salted. As the composition of wastewater is more complex, the existing experimental verification for simple system is no longer applicable.

The main reasons why it is difficult to apply dry salt formation techniques to complex salt systems are as follows: complex salts mean that there is a wide variety of anions and cations in the system. These involve complete ionisation of strong electrolytes, partial ionisation of weak electrolytes, ionic reactions, complex ion formation, precipitation and dissolution of salts. This results in uncertainty in the number of reactions in the system, uncertainty in the extent to which the reactions proceed and uncertainty in the physicochemical properties. Ultimately, the generation, diffusion, escape or accumulation of flammable, explosive, toxic and hazardous substances in complex salt systems during the drying and salt formation process cannot be determined and controlled. The amplification effect of reaction absorption and heat release in industrial application and the technical characteristics of high temperature of drying salt formation will lead to great insecurity and difficulty in control of the technology. Generally speaking, the new drying and salt formation process of complex wastewater system needs to be enlarged from small test to pilot test. However, if the research horizon is extended to isotope extraction, decommissioning of nuclear facilities and changes in production demand, etc., All the above conditions will lead to the continuous complex changes of wastewater components. If the study of new technology parameters is always used and clumsy and exhaustive experiments are used to recustomize the new complex system one to one, it will only cause a lot of waste of manpower, material resources and financial resources. Therefore, it can be seen that the bottleneck of drying salt formation technology to deal with wastewater with complex components is the lack of universality to solve the complexity of chemical reaction.

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2 Research methods

In this study, the innovation is to use Aspen Plus software to simulate and optimize drying salt formation. The complex electrolyte thermodynamic model was constructed according to the actual waste liquid and waste gas conditions of YD(medical isotope test reactor) project. Among them, ELENRTL physical property is selected as physical property.

2.1 Principle of material balance

According to the Law of Conservation, the general expression of material balance in the system is: Accumulation in the system = Input(F_{in})-Output(F_{out}) + Generation(G_R)-Consumption(C_R). Assuming the system is leak-free, there is the following formula:

$$\frac{dF}{dt} = F_{in} - F_{out} + G_R - C_R \qquad (1)$$

In the above formula, the term generated or consumed is the amount generated or consumed due to chemical reaction. The accumulation amount can be positive or negative. When the cumulative quantity in the system is not zero, it is called an unstable state. When the accumulation is zero, it is called stable state The steady state can be simplified as:

$$F_{in} = F_{out} - G_R + C_R \qquad (2)$$

2.2 Principle of energy balance

The material balance of the system is based on the law of conservation of energy, and the balance formula of energy is established. The energy balance expression of the system is: Input system energy = output system energy + accumulated system energy. The equipment in this device mainly includes reactor tower equipment, heat exchanger and fluid conveying machinery. The energy input into the whole production system mainly includes electric energy, fuel, chemical energy and enthalpy of materials(H_{in}). The output energy mainly includes the energy of generating steam and the enthalpy of the output material(H_{out}). According to the energy relationship in the system, the energy balance equation is listed as follows:

$$Q + W = H_{out} + H_{in} \qquad (3)$$

Where Q is the heat load of the equipment and W is the mechanical energy input to the system.

2.3 Process and chemical reaction system

The model includes the waste stream from seven production lines, the waste gas treatment system alkaline wash stream, the pH adjustment line and the salt solution adjustment line. The treatment unit includes recirculating spray alkaline scrubbing of NOx gas, mixing, drying to salt and condensation cooling. The model was constructed and the reactions considered are shown in Figure 1 and Table 1.

Table 1. Simulation model considers reactions and details

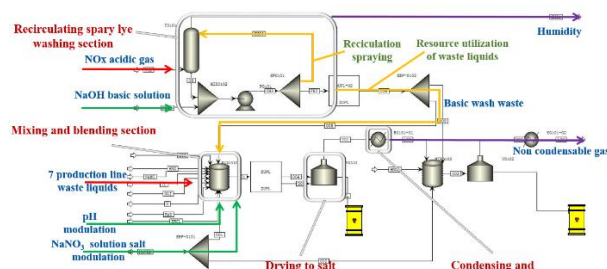| Reactions	Control limitations
$2NO_2 + 2OH^- \leftrightarrow NO_2^- + NO_3^- + H_2O$	Dynamic
$2NO_2^- + O_2 \leftrightarrow 2NO_3^-$	
$HNO_3 + H_2O \leftrightarrow H_3O^+ + NO_3^-$	
$HCL + H_2O \leftrightarrow CL^- + H_3O^+$	
$HNO_2 + H_2O \leftrightarrow H_3O^+ + NO_2^-$	
$NH_3 + H_2O \leftrightarrow OH^- + NH_4^+$	
$2H_2O \leftrightarrow OH^- + H_3O^+$	
$NH_4NO_3(s) \leftrightarrow NH_4^+ + NO_3^-$	Thermodynamic
$NaOH(s) \leftrightarrow Na^+ + OH^-$	
$NH_4CL(s) \leftrightarrow NH_4^+ + CL^-$	
$NaCL(s) \leftrightarrow Na^+ + CL^-$	
$Na^+ + OH^- + H_2O \leftrightarrow NaOH \bullet H_2O(s)$	
$NaNO_3(s) \leftrightarrow Na^+ + NO_3^-$	
$NaNO_2(s) \leftrightarrow Na^+ + NO_2^-$	
$NaNO_3 \rightarrow Na^+ + NO_3^-$	
$NaOH \rightarrow Na^+ + OH^-$	
$NH_4NO_3 \rightarrow NH_4^+ + NO_3^-$	
$NaNO_2 \rightarrow Na^+ + NO_2^-$	

Fig. 1. Thermodynamic electrolyte model process flow.

3 Results and discussion

3.1 Effect of electrolyte system and model validation

According to the experimental data of Chao et al.[5], the electrolyte simulation model is verified by taking sodium nitrate, the main component of crystal, as the system. The validation results are shown in Figure 2.
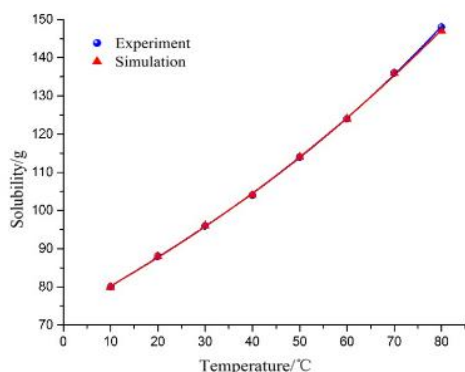
Fig. 2. Verification of the solubility of sodium nitrate.

The graph shows a high degree of agreement between the simulation results and the experimental results. In addition, the removal efficiency of NOx by circulating alkali washing and spraying in acid gas is more than 99.9%. Therefore, it shows that the electrolyte simulation model built in this study has some prediction accuracy. Next, this section simulates a boric acid system[5] containing five electrolytes. The results are shown in Figure 3.

The graphs express the simulated trends in approximately the same way as the experimental results. In particular, the start and end phases of microwave heating are highly consistent. However, there is still a gap between the two processes in the later stages of heating. In the actual heating process, there is a problem of uneven heating and heat loss in the later stages of microwave heated crystallisation. This is due to the growth and accumulation of crystals resulting in moisture in the gaps of the crystal particles is limited by heat transfer.
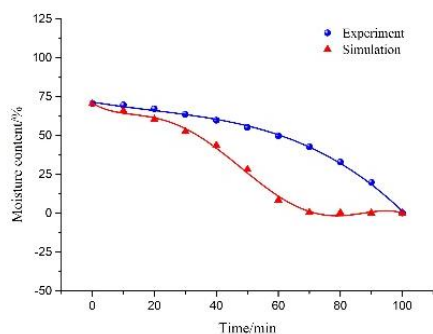

Fig. 3. Crystallisation verification of complex boron-containing electrolyte systems.

In summary, if the microwave heating crystallisation process needs to reduce heat loss and improve energy efficiency. As far as possible, a reasonable trade-off should be made between phased feedstock and the heating process. Controlling the water content to reach the standard temperature within about 20 minutes can effectively reduce the energy loss of microwave heating.

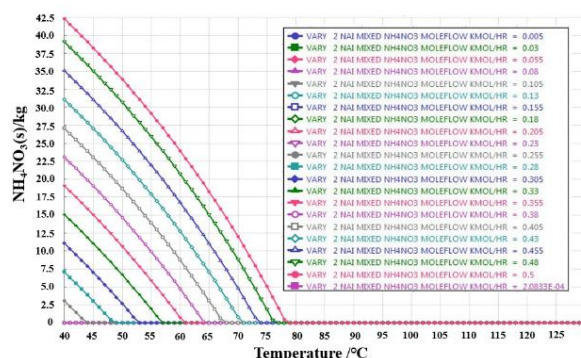## 3.2 Effect of temperature on the production of dangerous crystals

Fig. 4. The effect of temperature on NH_4NO_3 crystals.

NH_4NO_3 crystals are extremely unstable and decompose easily at high temperatures. A sensitivity analysis regarding the production of NH_4NO_3 crystals is shown in Figure 4. The picture shows that NH_4NO_3 crystals are mainly produced in the temperature range below 80°C. Meanwhile, the amount of NH_4NO_3 crystals produced decreases with increasing temperature until they disappear completely. Due to the pyrolytic nature of NH_4NO_3 crystals, it decomposes at high temperatures to produce NH_3 gas. If NH_4NO_3 crystals are produced during the drying to salt process, this will result in the decomposition of NH_4NO_3 crystals at high temperatures and during the crystal build-up. Further, the salt blocks produced by the crystal build-up will have a large void ratio, difficulty in achieving the water content and a low density of the salt blocks. However, due to the inevitable process of rising from low to high temperatures in the dry salt formation technique. Therefore, the solution proposed according to the electrolyte simulation model is to avoid NH_4NO_3 crystal production by controlling the NH_4^+ content, NO_3^- content and pH of the feedstock waste stream.
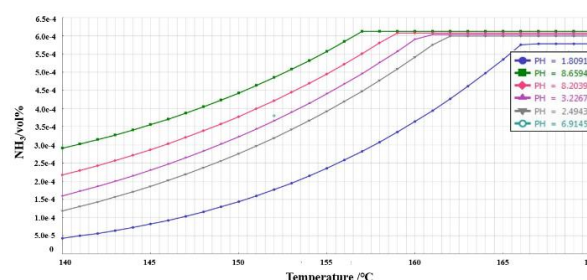
3.3 Effect of pH on NH3 concentration

Fig. 5. The effect of pH on the concentration of NH_3 in secondary steam.

The effect of ph on the concentration of NH_3 in the vapour produced by the drying to salt process is shown in Figure 5. The images show that the concentration of NH_3 increases and then levels off with increasing temperature. In addition, the concentration of NH3 also increases with increasing pH and tends to level off at a lower temperature point. NH_3 explosion limit of 16-25 vol%. The concentration of NH_3 produced by the present

electrolyte system is less than 1%, therefore it can be concluded that there is no explosion risk in the present study system. However, in order to avoid unpredictable escape and accumulation of NH_3, this process system is still equipped with NH_3 concentration monitoring and a nitrogen dilution interlock.

For the electrolyte system in this study, in addition to ensuring that the water content of the stacked crystal blocks is less than 1%. It is also necessary to avoid NH_4NO_3 crystal production. Furthermore, according to practical engineering experience alkaline waste streams are prone to foaming when heated. This in turn will lead to the purification effect of the waste stream being affected. In summary, a heating temperature of 152°C and a pH of 6.9 is suitable, taking into account energy consumption, safety and purification factors.

4 Conclusion

The current dry salt formation technology has good development momentum and broad application prospects. In this study, the thermodynamic electrolyte simulation model established in this study is verified to be accurate in prediction. On this basis, the optimum operating parameters of drying salt formation technology are determined. These include the modulation of temperature, pH and salt composition. Furthermore, through a sensitivity analysis of the technology, the study has improved the safety and optimisation of the technology and the associated process configuration. This study provides theoretical guidance for the research ideas and in-depth research of drying salt formation technology.

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