# Application of METSIM in Process Design of the Cleaner Chromate Production Using Sub-molten Salt

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***Abstract***

*The cleaner chromate production process using sub-molten salt has been successfully simulated using METSIM in order to evaluate the mass balance, energy consumption, and other conditions necessitate for the process scaling up. Based on the simulation results, the mass and heat balance of every operation unit are obtained, providing valuable reference for the process design. Further, the heat exchange network optimization using pinch technology is performed, enabling the reduction of the heat and cool energy consumption by 31.5% and 31.7%, respectively.*

***Key words****: sub-molten; process of chromate; METSIM; process simulation; pinch technology; optimization*

## 1. Introduction

Chromium compounds are essential to many industries. Currently, the main manufacturing process is non-calcium roasting. In this process, however, the resource and energy utilization efficiency are quite low(<80%), and 2.5~3tonnage chromium-containing residues are produced for manufacturing 1 tonnage of chromate, creating serious pollution problems [1].

In order to realize green production of chromate, a cleaner manufacturing process using sub-molten salt (SMS) technology has been developed by the Institute of Process Engineering, Chinese Academy Sciences. The recovery of chromate can reach 95%, and the residues produced can be reduced to one fifth in comparison with the traditional process. A demonstration project with an annual production capability of 10,000 tonnage of potassium dichromate has been built in Henan Province, China. The technology has exhibited promising perspective for further industrialization.

Accurate mass and energy balances are critical for the process development, and are essential for the designing and scaling the process equipments. With the aid of processing simulation software, the calculation of mass and energy balances can be realized in a routine manner with excellent accuracy, significantly alleviating the work intensity of process designers.

Currently, much software has been developed for use [2-4]. Software developed for petrochemical industries, such as ASPEN PLUS [5] and PRO Ⅱ [6], have recently been applied to metallurgical process modeling. Although some of the operation units can be well described using the above mentioned software, the complexity of the process due to the involvement of solid particles limits its application. Further, typical petrochemical process

modeling software usually does not contain databank regarding minerals and inorganic compounds, significantly depreciating its application in the process designing.

In order to facilitate the process development of the mineral processing industry, software such as SysCAD, IDEAS, and METSIM [7] have been developed, capable of performing static and dynamic modeling of most mineral processing operation units [8]. And METSIM, which offers a wide range of capabilities and features tailored to the metals industry, has excelled in performing mass and energy balances.

Hernandez, *et al.*, [9] have simulated an industrial process for extracting arsenic from solutions through scorodite crystallization at 70 ℃. The simulated process allows for the analysis of different evaporation ratios, determining the mass and energy balances and the quality of the products and residues, thus providing important information for potential industrial applications.

Chanveha, *et al.*, [10] have developed a model of a primary smelting reactor to estimate heat loss and phase distributions of matte and slag. The model predictions are validated with plant data, and good agreement is observed, which is used to analyze the influence of the feed rates of copper concentrate, oxygen, silica flux, and revert on the primary smelting reactor performance.

In summary, METSIM has been believed to be one of the top choices for mineral treatment process designing. In this regard, the application of METSIM in calculating mass and energy balances for a typical hydrometallurgy process has been demonstrated, and based on the results, the heat network is optimized simultaneously in this paper.

## 2. The cleaner process of chromate production

The SMS unconventional media is defined as an ionized media of highly concentrated alkali metal hydroxides solution. It is capable of providing highly active oxygen anion and thereby intensifying reaction and mass transfer process. A schematic flow sheet for a typical chromite ore treatment process is shown in Figure 1. In this process, the operation unites include leaching, filtration, separation, and evaporation. However, leaching and evaporation are the main energy consumption units, so modules including leaching and evaporation are tested. Modules are developed using METSIM software to calculate mass and energy balances.

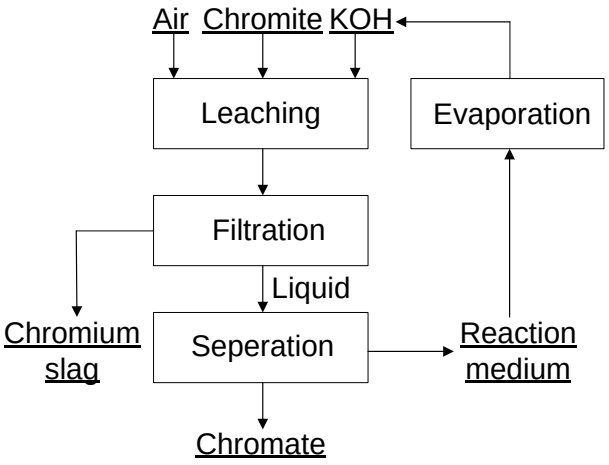



**Figure 1. The cleaner process of chromate production**

# 3. Process simulation using METSIM

## 3.1. Mass balance

The detailed process of evaporation and leaching is shown in Figure 2. The evaporation unit includes preheat, evaporation, and alkali boiling, which concentrates 298 K 50%($\omega$) lye to 593 K 70%($\omega$) lye.

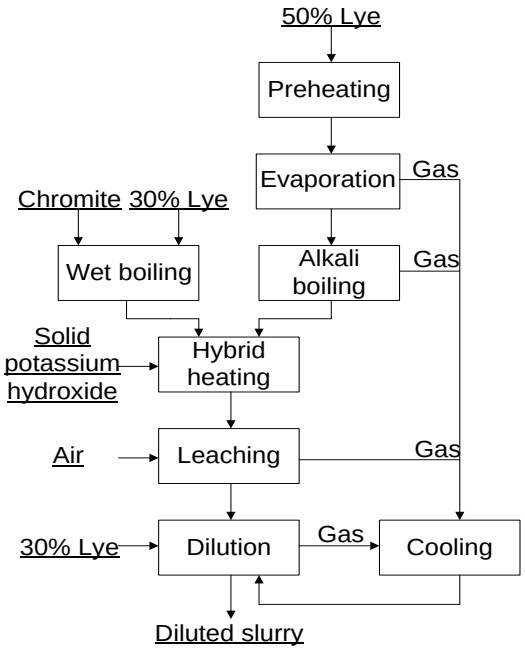



**Figure 2. The process of evaporation and leaching**

Leaching is modeled using a default reactor object, and the reactions that occur in the reactor for oxidation of slag are described as follows:

$$4KOH+Cr_2O_3+1.5O_2=K_2CrO_4+H_2O, \quad (1)$$

$$2KOH+CO_2=K_2CO_3+H_2O, \quad (2)$$

$$2KOH+Al_2O_3=2KAlO_2, \quad (3)$$

$$2KOH+SiO_2=K_2SiO_3. \quad (4)$$

The leaching rates of vanadium, aluminum, and silicon are controlled to be 96%, 100%, and 100%, respectively according the previous experimental results, and the addition of KOH is controlled by the mass balance. Addition of air is controlled to be stoichiometric according to the chemical reaction listed above.

The dilution is modeled using default tank object with agitator. The input criteria for the tank object are set to ensure the weight fraction of potassium hydroxide to be 50% after dilution.

In this article, the simulation based on the reference of an annual capacity of 15,000 tons $Cr_2O_3$, and the process is designed to operate 24 hours a day and 300 days a year. The main components of chromite ore are shown in Table 1. 30% lye and 50% lye come from industrial data, shown in Table 2.

**Table 1. The composition of chromite**

| Component (%, $\omega$) | $Cr_2O_3$ | $SiO_2$ | CaO | MgO | $Fe_2O_3$ | $Al_2O_3$ | $H_2O$ | Total |
|---|---|---|---|---|---|---|---|---|
| Chromite | 42.6 | 2.7 | 0 | 10.0 | 27.6 | 12.1 | 5.0 | 100 |

**Table 2. The composite of potassium hydroxide solution with 30% and 50% KOH (%, $\omega$)**

| Component | $H_2O$ | KOH | $K_2CrO_4$ | $K_2CO_3$ | $K_2SiO_3$ | $KAlO_2$ | Total |
|---|---|---|---|---|---|---|---|
| 30% Lye | 64.9 | 30 | 2.0 | 2.96 | 0.0014 | 0.178 | 100 |
| 50% Lye | 30.8 | 50 | 0.2 | 7.0 | 0.5 | 11.5 | 100 |

Note: 30% lye and 50% lye stands for the aqueous solution after chromate separation.

The model developed using METSIM is shown in Figure 3, and the mass balance results obtained is shown in Table 3. From Table 3, it can be seen that the maximum deviation is 5.99%, and the average deviation is only has 0.8%, confirming that the model is appropriate for simulation such a process.

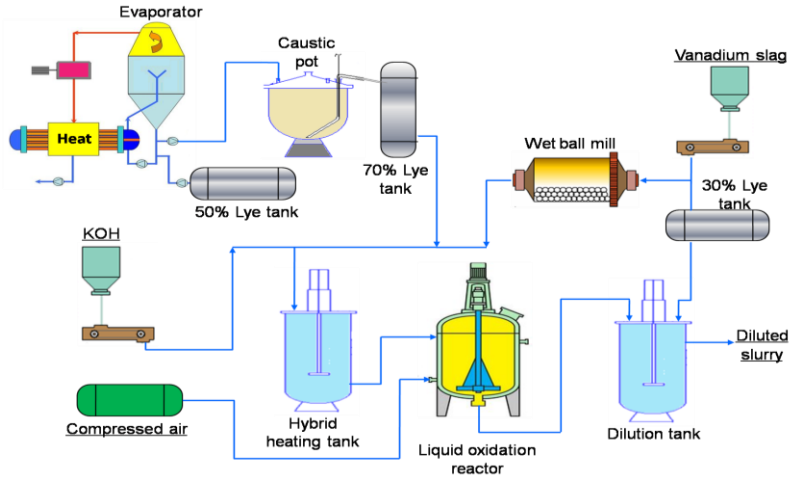



**Figure 3. The model of evaporation and liquid phase oxidation units using METSIM**

**Table 3. The result of mass balance**

| Diluted slurry | | Simulation (kg/h) | Experiment (kg/h) | Deviation (%) |
|---|---|---|---|---|
| Liquid phase | $H_2O$ | 18955.9 | 20163.5 | 5.99 |
| | KOH | 23356.0 | 22653.3 | 3.0 |
| | $K_2CrO_4$ | 90.3 | 90.6 | 0.3 |
| | $K_2CO_3$ | 3171.5 | 3171.5 | 0.0 |
| | $K_2SiO_3$ | 232.4 | 232.4 | 0.0 |
| | $K_2AlO_2$ | 5225.9 | 5223.8 | 0.04 |
| Solid phase | $K_2CrO_4$ | 5735.4 | 5729.6 | 0.1 |
| | $K_2CO_3$ | 275.4 | 275.2 | 0.07 |
| | $K_2SiO_3$ | 311.8 | 311.6 | 0.06 |
| | $K_2AlO_2$ | 423.7 | 424.4 | 0.2 |
| | $Cr_2O_3$ | 63.8 | 63.8 | 0.0 |
| | MgO | 499.1 | 499.1 | 0.0 |
| | $Fe_2O_3$ | 1377.6 | 1377.6 | 0.0 |

### 3.2. Energy balance

The energy change in the process is calculated using the following Equation

$$\Delta H_T = \Delta H_{298.15} + \int_{298.15}^{T} \Delta C_p dT, \quad (5)$$

$\Delta H_T$ and $\Delta H_{298.15}$ stand for the enthalpy value at $T$ and 298.15 K, respectively. T is the tempreture with the unit K, and $\Delta C_p$ is the heat capacity, whose unit is J/(mol·K). From Equation (5), we can see that the heat capacity is crucial in calculating enthalpy. Because SMS media features high alkali concentration and high temperature, the heat capacity is deficient. In order to perform the energy balance of the process, the heat capacity of SMS media must be obtained first.

Wang, *et al.*, [11] have studied the heat capacity variation of potassium hydroxide solutions. From his study, it is conclude that temperature has negligible effect on the heat capacity, but the potassium hydroxide concentration has significant effect on the heat capacitywhen the weight fraction of KOH is over 50%. So a equation for calculating potassium hydroxide solution heat capacity is obtained by nonlinear fitting.

$$C_p = 0.375\omega^2 - 0.8\omega + 0.27625, \quad (6)$$

where $\omega$ denotes the weight fraction of KOH($\omega$, %). In METSIM, the heat capacity is related to temperature, so we need to translate Equation (6) according to the boiling point of the potassium hydroxide aqueous. Frank [12] proposed that heat capacity of a component in aqueous can be calculated by

$$C_{p,KOH} = C_p - n_1 C_{p,H_2O}/n_2, \quad (7)$$

where $n_1$ is the moles of water, and $n_2$ is the moles of KOH, so a new Equation is achieved.

$$C_{p,KOH} = -1221.574 + 3715\times10^{-3}T + 297.121\times10^{5}T^{-2} - 3140\times10^{-6}T^{2}. \quad (8)$$

The Equation(8) is added to METSIM, and the energy balance is obtained, and the results are shown in Table 4.

**Table 4. The result of energy balance**

| Operation unit | Preheating | Evaporation | Alkali boiling | Hybrid heating | Leaching |
|---|---|---|---|---|---|
| Value ($\times10^7$ kJ/h) | 0.37 | 2.26 | 0.54 | 0.36 | 1.00 |

To test the heat capacity, the energy consumption of evaporation unit is further estimated using the data from Chlor-alkali industry manual, and the date we used is shown in Figure 4 and Figure 5. The estimated result is shown in Table 5.

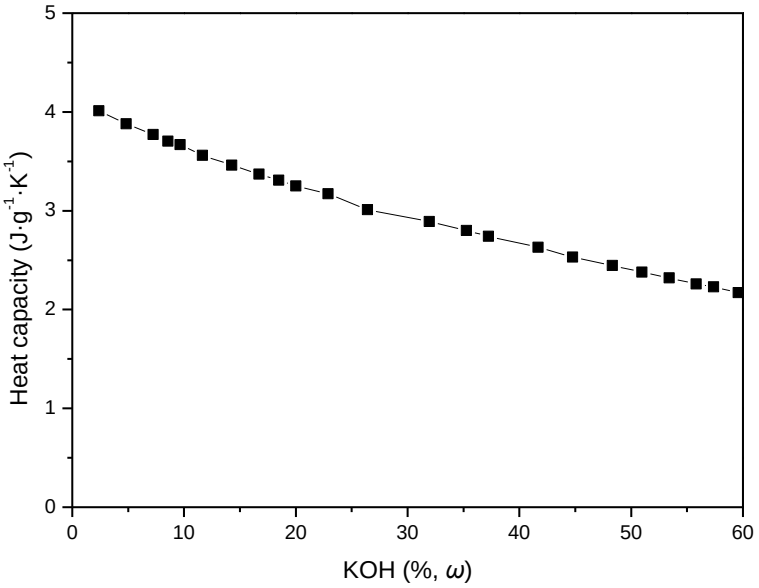



**Figure 4. The heat capacity of potassium hydroxide solution at 291 K**

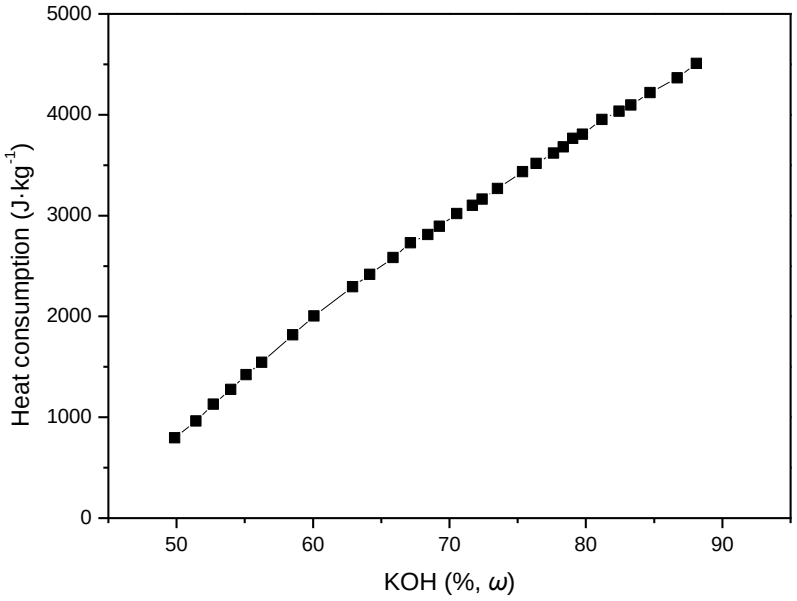



**Figure 5. The heat consumption of potassium hydroxide solution when it is concentrated**

**Table 5. The contrast of simulation and estimation about concentration unit ($\times 10^6$ kJ/h)**

| Operation unit | Preheating | Evaporation | Alkali boiling |
|---|---|---|---|
| Simulation | 3.72 | 22.55 | 5.40 |
| Estimation | 5.35 | 23.68 | 8.07 |

From Table 5, it can be seen that the simulation results are consistent with the estimated results, suggestting that the heat capacity utilized is reasonable and the energy balance from METSIM can offers a good reference.

From Table 4, it is seen that the liquid oxidation and evaporation units have large energy consumption. At the same time, much high grade steam is produced in this process. By proper process design, energy consumption can be reduced, improving the economics of the new process.

### 3.3. Energy optimization

The pinch technology is chosen to optimize the process. Four hot streams and six cool streams are picked from the process: hot streams: (1) Evaporation vapor; (2) Alkali boiling vapor; (3) Leaching vapor; (4) Dilution vapor; cool streams: (1) Compressed air; (2) Lye preheating; (3) Lye evaporation; (4) Lye boiling; (5) Hybrid heating; (6) Leaching. The composite curve is gained, shown in Figure 6.

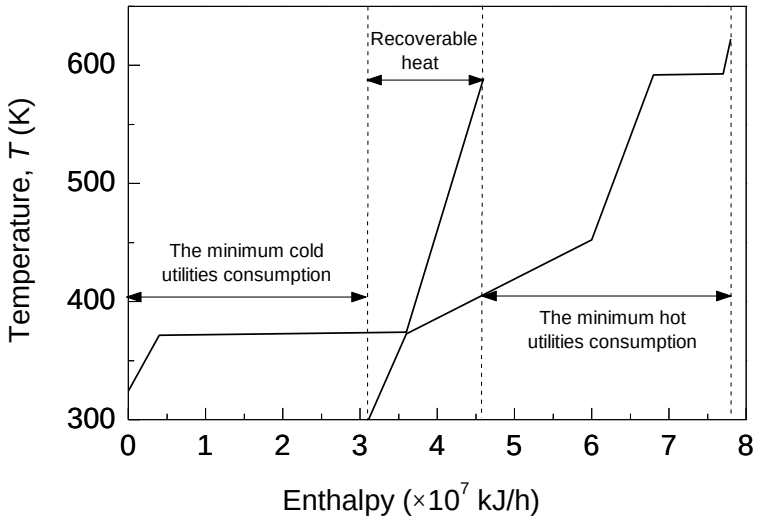
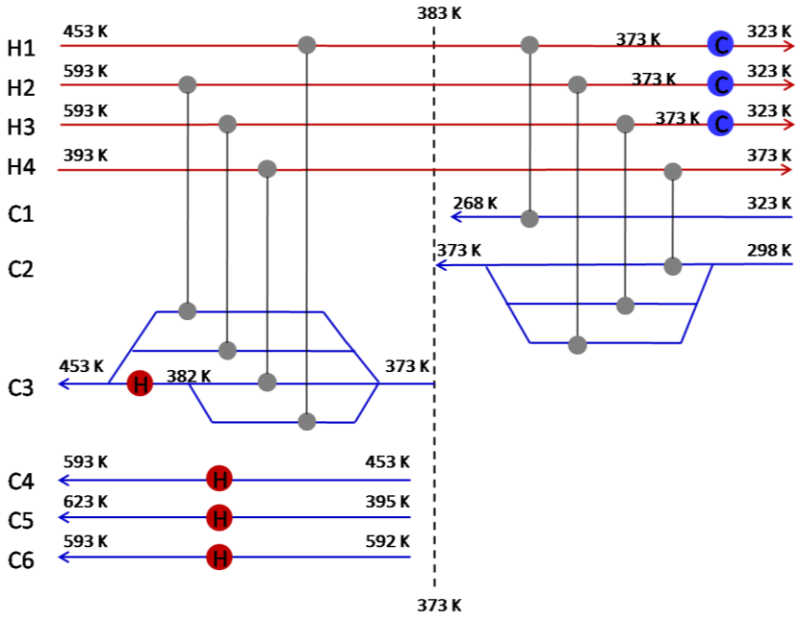



**Figure 6. The composite curve of the heat exchanger network**

From Figure 6, it is concluded that the minimum hot and cool utilities are $3.18\times10^7$ kJ/h and $3.14\times10^7$ kJ/h, respectively. Based on this result, the heat exchanger network is matched, shown in Figure 7 The matching rules are: (1) $N_{in} \geqslant N_{out}$; (2)$C_{p,in} \geqslant C_{p,out}$, $N$ stands for the total stream numbers, and $C_p$ is the heat capacity flow rate.




H1. Evaporation vapor H2. Alkali boiling vapor H3. Leaching vapor
H4. Dilution vapor C1. Compressed air C2. Lye preheating
C3. Lye evaporation C4. Lye boiling C5. Hybrid heating
C6. Leaching

**Figure 7. The match result of the heat exchanger network**

After optimization, the cool and hot utilities are reduced: $1-3.14\times10^7/4.60\times10^7=31.7\%$, $1-3.18\times10^7/4.64\times10^7= 31.5\%$.

## 4. Conclusion

The accurate mass and energy balances are critical for hydrometallurgical process development, and are essential for the designing and scaling the process equipments. In this article, METSIM has been proved to be appropriate to the cleaner process with sub-molten salt technology. With the aid of processing simulation software-METSIM, the calculation of mass and energy balance can be realized in a routine manner with excellent accuracy, significantly alleviating the work intensity of process designers.

From the mass and energy balances results, the major components in streams and their mass flow can be clearly presented from the flowsheet. Based on the model, the processing conditions including the amount of wash water, the split ratio, and evaporation ratio can be changed with great flexibility, providing information for the practical process design.

The optimization of the heat exchanger network improves its economic benefits. Based on the match result, the cool and hot utilities are reduced by 31.7% and 31.5%, respectively, without changing the original devices, which provides technical support for industrial application.

Although in this study, only the mass and energy balances have been calculated, the models established in this study can further be utilized for process design, equipment estimate, and economic evaluation, which are very important in a process design. In summary, the

simulation using METSIM allows process designers to evaluate a hydrometallurgy process based upon experimental data and reasonable assumptions, providing important information for potential industrial applications.

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