Thermodynamics of P_2O_5-Containing Slag and the Gas-Slag Equilibrium in the Waste Melting Process

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ABSTRACT The parameters of Na_2O-P_2O_5 and Na_2O-SiO_2 systems used in the cell model have been assessed. The cell model was used to calculate the activities of components in the slag phase, and the gas phase was treated as ideal in simulations of the waste melting process. The calculated slag and gas compositions were compared with plant data and satisfactory agreement was obtained. The calculated results show that 73% P in charged materials entered the gas phase and were later deposited out on the wall of the waste heat boiler as H_3PO_4, contributing to the corrosion observed there. The addition of CaO to the process was found to promote fixation of P in the slag phase, thus reducing the corrosion of the waste heat boiler.

1 Introduction

In recent years, the awareness of the necessity to preserve the environment and to conserve our limited natural resources has led to increasingly strict requirements for recycling wastes. The waste melting process described in this paper is a type of process which enables a considerable reduction of volume, stabilization and utilization of sewage sludge [1]. In this process, dewatered sludge cake, coke and flux are charged into the melting furnace where the combustibles contained in the sludge are burned on the coke bed. Non-combustibles are melted down and recovered in the form of non-hazardous slag which is safely used as road paving material and building material. The gas-slag reactions are of considerable industrial interest. An understanding of these reactions can help us to predict and control the distribution of elements and then to optimize the industrial operations. In this work, the waste melting process was simulated through the multi-components and multi-phases equilibrium method. The calculated results on slag and gas compositions are compared with plant data.

2 Industrial Trial

An industrial trial of the process was carried out in sludge treatment plant A in 1998. The charged materials as well as products such as sludge cake, blowing air, exhaust gas and dust were sampled and then chemically analyzed. The input rate of charged materials and the temperature of gas were also recorded. The compositions and input rates of the charged materials are listed in Table 1[2].

3 Simulation System

The complexity of the industrial process generally necessitates that a number of assumptions be made in order to simplify the modeling process. The most important assumption is that the melting system is in both chemical and thermal equilibrium. In this case, it is assumed that all the charged materials during a given time step are in equilibrium. In the industrial furnace, the temperature is unevenly distributed. In order to simulate the process accurately and simply, the furnace was divided into three reaction zones. These zones were simulated sequentially. The melting furnace is illustrated in Fig.1. The system is assumed to consist of a gas phase, a

slag phase and condensed phases. According to the analytic results of industrial charged materials, the system contains 16 elements, namely, Pb, Zn, Al, Ca, Fe, Mg, P, K, Na, Si, C, S ,Mn, H, N and O, and the components of each phase are assumed to be as follows:
Gas phase: N_2, NH_3, CH_4, S_2, ZnS, CS, CS_2, SO, SO_2, CO, CO_2, SO_3, Zn, H_2S, H_2, HS, H_2O, MnO, Na, MgO, Na_2O, Mg, NO_2, N_2O_5, K, K_2O, FeS, P_4O_{10}, CaH, KH, NaH, Na_2SO_4, K_2SO_4, P_4, SiO, PN, SN, KCN, NaCN, CN, COS, $K_2(CN)_2$, C_2N_2 and P_4S_3
Slag phase: Al_2O_3, SiO_2, P_2O_5, CaO, FeO, Fe_2O_3, Na_2O, MgO, MnO, K_2O and ZnO
Condensed phase: Na_2CO_3, Na_2SO_4, Na_2SO_3, K_2SO_4, K_2SO_3, KH_2PO_4, H_3PO_4, ZnS, ZnO, $ZnSO_4$, SiO_2, Al_2O_3, $Na_4P_2O_7$, $CaCO_3$, FeO, Fe_2O_3, SiO_2, $Ca_3P_2O_8$, $Ca_2P_2O_7$, K_2CO_3, Zn, FeS, MgS, CaS, Al_2S_3, Na_2S, C, S, Fe_3C, P, CaC_2, Al_4C_3, $Mg_3P_2O_8$, MgC_2, SiC and K_2S
During the calculation, the gas phase can be treated as ideal while the molten slag phase is not so. In thermodynamic studies, it is important to choose an appropriate solution model to calculate the activities of components in the slag phase. As listed above, the molten slag phase is a mixture of oxides. Among the models concerning slag, the cell model and the modified quasi-chemical model are now widely used in the calculation of oxide slag[3-6] . These two models are all extended to poly-anionic and multi-component systems. The parameters which will be used in the modified quasi-chemical model of all binary subsystems in 11 components, namely, Si_2O-CaO-Al_2O_3-FeO-MgO-MnO-Na_2O-K_2O-TiO_2-Ti_2O_3-Zr_2O-S, have been evaluated[7]. The cell model parameters for the P_2O_5-SiO_2-Cr_2O_3-Al_2O_3-Fe_2O_3-CrO-FeO-MnO-MgO-CaO system have been assessed by Gaye *et.al*[8]. According to the industrial report, the content of P in slag is about 2 wt%, so P_2O_5 should be considered in the slag system. In the present work, the cell model was chosen to calculate the activities of components in sludge melting slag.

4 Assessment of the Parameters Used in the Cell Model

Cell model uses two kinds of energy parameters to describe the formation of cells (W_{ij}) and the interaction between cells (E_{ij}) and give an expression for activity coefficient in liquid slags as a function of temperature and composition.

Systems Containing Na_2O
Na_2O is included in the slag system. The parameters of the Na_2O-P_2O_5 system used in the cell model are still lacking. In order to simulate the process precisely and to study the influence of Na_2O on the behavior of P_2O_5 in slag, the parameters of Na_2O-P_2O_5 have been optimized: W_{NaP} =-132KJ, E_{NaP}=-165KJ. Due to the high content of SiO_2 in the slag phase, the effect of SiO_2 on Na_2O is prominent. Adding the parameters of the Na_2O-SiO_2 system to the model will make the simulated results become closer to the practical ones. Through the assessment, the following parameters are obtained: W_{NaSi}=-92 KJ, E_{NaSi}=45 KJ. The validity of the assessment is illustrated in Fig. 2 and Fig. 3, respectively. As shown in Figs. 2 and 3, the general agreement between model prediction and experimental values is rather good.

Activity Coefficient of K_2O in Slag
The measured activity data for the K_2O binary system are not available so far. This makes it impossible to optimize the model parameters between K_2O and other species and to incorporate K_2O in a non-ideal solution model. Turkdogan derived the activity of K_2O in the K_2O-CaO-MgO-SiO_2-Al_2O_3 slag system. The following coefficient-composition relationship for K_2O was derived from Turkdogan's results by H.-J. Li et al.[9]

$$\gamma_{K2O} = 2.86\times10^{-10}\,(\text{wt pct } K_2O)^2/X_{K2O} \qquad (1)$$

The gas-slag equilibrium in the sludge melting furnace was calculated by using a commercial software package-ChemSage, incorporating the cell model for the slag phase and the empirical expression (1) for K_2O.

5 Results and Discussion

As mentioned previously, the melting furnace was divided into three parts which were simulated sequentially.

The First Reaction Zone

Due to the high temperature in the furnace and the charge of the sludge cake from the upper part of the furnace, all of the water in the cake is assumed to have already evaporated and reacted with other reactants in the second zone before the cake reached the coke bed. The sludge ash was combusted and melted down to form the slag on the coke bed. The calculated compositions of the slag and gas phase in this zone with the relevant plant data are listed in Tables 2 and 3, respectively. The comparisons show that the calculated contents of elements in the slag are in good agreement with those of the plant data. It's very difficult to sample the gas in this zone during the melting process. For this reason, the calculated composition of the gas phase can't be directly compared with the relevant plant data. The calculated results show that the main components of gas are N_2, H_2 and CO. Because the first zone is under strong reduction conditions, most of P in gas is assumed to exist as a form of PN which might be formed through the following two reactions.

$$2P_2O_5 + 10C = P_4 + 10\ CO \quad (2)$$

$$P_4 + 2N_2 = 4PN \quad (3)$$

The distribution of phosphorus among components is shown in Table3. The amount of P_4O_6 in gas is small. The condensed phase didn't appear in this step from the viewpoint of thermodynamic calculation.

The Second Reaction Zone

The water vaporized from the cake, air 23 and the gas from the first zone mixed together and reacted in the second reaction zone at a temperature of about 1373 K. The calculated gas and dust compositions are shown in Tables 4 and 5, respectively. Due to the input of air 23, H_2O and CO_2 are calculated to appear predominantly in the gas phase instead of H_2 and CO in the first zone. PN was also oxidized to P_4O_{10}. Excessive oxygen in the gas is about 2.2 Vol%. The Na and SiO in the gas phase deposited out as a form of $Na_4P_2O_7$ and SiO_2 dust at the same time by reaction (4) and reaction (5), respectively.

$$4Na + P_4O_{10} + O_2 = 2Na_4P_2O_7 \quad (4)$$

$$2SiO + O_2 = 2SiO_2 \quad (5)$$

The Third Reaction Zone

All of the gas and dust from the second zone are assumed to be the reactants in the third zone. Boiler tubes were inserted in the upper portion of the furnace to absorb waste heat. The temperature in this zone was controlled at about 1063K by introducing cooled gas into the furnace. The calculated equilibrium composition of the gas and condensed phase are listed in Tables 6 and 7, respectively. Zn and K_2SO_4 in the gas from the second zone were deposited out as $ZnSO_4$ and K_2SO_4. It is clear that the main components such as CO_2, O_2, H_2O and N_2 in the gas phase agree with the measured data.

As the exhaust gas coming out of the furnace is very hot, the heat was recovered by an air pre-heater and a waste heat boiler. The temperature of the exhaust gas was decreased to 943 K and 473 K, in the pre-heater and boiler, respectively. Thermodynamic simulation of conditions in the air pre-heater and the waste heat boiler was also carried out. The results show that although there is no deposition at the temperature of air pre-heater, nearly all of the

P in the exhaust gas was deposited out as H_3PO_4 at 473 K through reaction (6) on the wall of the waste heat boiler, contributing to the corrosion observed there.

$$P_4O_{10} + 6H_2O = 4\ H_3PO_4 \qquad (6)$$

Effects of CaO on the Distributions of P in the Melting System

It is well known that high basicity of slag can improve the phosphorus capacity in the slag. According to the interaction parameter of Ca^{2+} and P^{5+} which was assessed by Gaye[4], the formation energy of Ca-O-P is –73.59 KJ. It is clear that the Ca-O-P pair is easily formed. The addition of CaO helps decrease the activity coefficient of P_2O_5 in slag. Although the formation energy of Na-O-P, which was assessed as being –165 KJ by the author is more negative than that of Ca-O-P, the use of Na_2O causes considerable difficulty in practice due to the erosion of refractories and the evaporation of Na_2O. The melting process was simulated under the situation of charging different amounts of CaO into the furnace. The calculated results are shown in Fig. 4. The P increases in slag with increasing CaO content, as expected. When the basicity of slag increases to 1.3, nearly 50% P enters the slag phase. The addition of CaO to the process was found to be an effective way to fix more phosphorus in the slag, which alleviates the corrosion of the waste heat boiler by H_3PO_4.

6 Conclusion

The parameters of Na_2O-P_2O_5 and Na_2O-SiO_2 systems which were used in the cell model have been assessed. These parameters, combined with other published cell model parameters and the empirical expression of the activity coefficient of K_2O, were used in the cell model to calculate activities for species in the sludge melting slag while the gas was treated as ideal. The calculated compositions of slag and exhaust gas from the melting furnace show good agreement with the plant data. This also means that simulating the sludge melting process through the multi-component and multi-phase equilibrium method is reasonable and effective.

From the simulation results, it is clear that nearly 27% P enters the slag phase. The remainder, that was in the gas phase, will be deposited later in the form of H_3PO_4 in the waste heat boiler. P that precipitates on the wall of the waste heat boiler as H_3PO_4 contributes to the corrosion observed there.

The addition of more CaO to the process was found to promote fixation of P in the slag phase, resulting in a reduction of the corrosion of the waste heat boiler.

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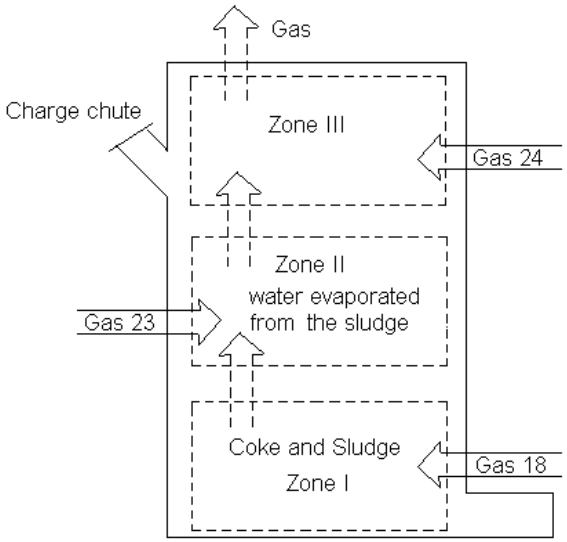

Fig. 1 Schematic diagram of melting process

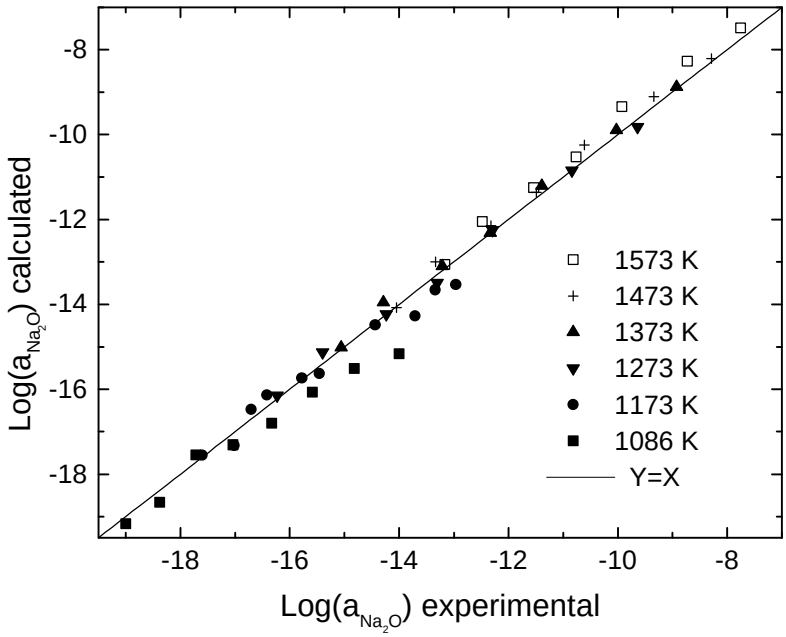

Fig. 2 Comparison of experimental and calculated Na_2O activity in the system Na_2O-P_2O_5[10]

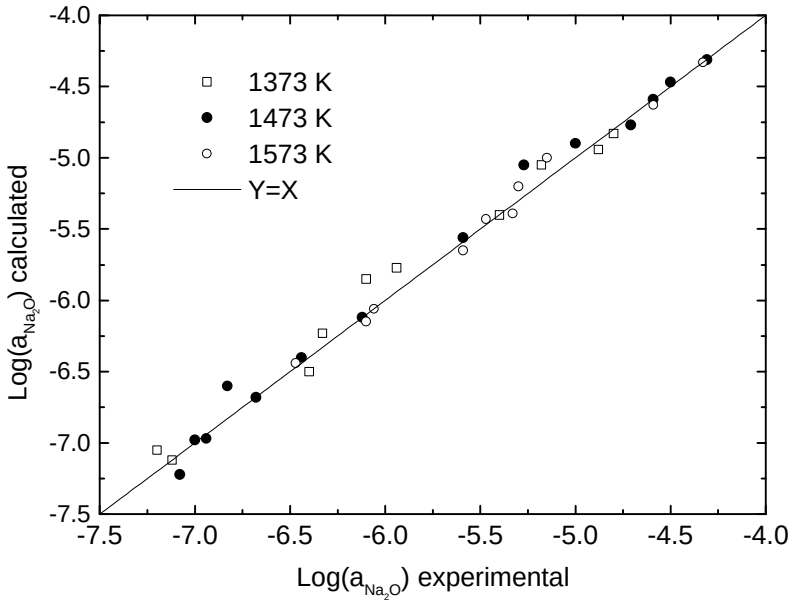

Fig. 3 Comparison of experimental and calculated Na_2O activity in the system Na_2O-SiO_2[11]

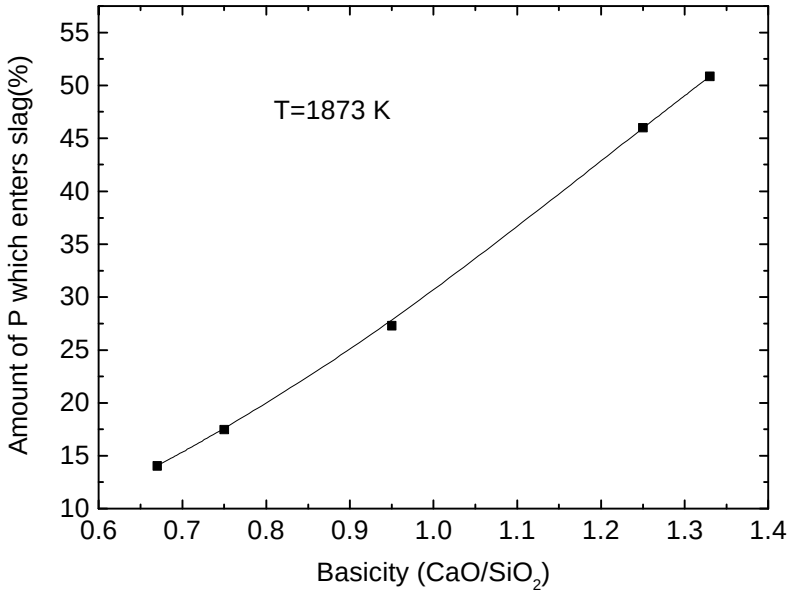

Fig. 4 Effect of CaO on the distribution of P in slag

Table 1. Compound compositions in charged materials

	Input gas 18	Input Gas 23	Input Gas 24	Lime Stone	Cake	Coke
Unit	mol/min	mol/min	mol/min	mol/min	mol/min	mol/min
Pb	0	0	0	0	0.0006	0
Zn	0	0	0	0	0.19	0
Al	0	0	0	0.018	7.84	5.48
Ca	0	0	0	7.82	0.16	0.16
Fe	0	0	0	0.01	2.64	0.75
Mg	0	0	0	0.18	1.55	0.097
Mn	0	0	0	0	0.06	0
P	0	0	0	0	6.30	0.082
K	0	0	0	0	1.44	0.2
Na	0	0	0	0	0.84	0
Si	0	0	0	0.07	19.98	8.18
C	0	0	0	0	258.6	326.6
S	0	0	0	0	1.36	0.06
O_2	286	401	81	0	0	0
N_2	1075	1510	304.83	0	0	0
H_2O	36	106	10.33	0	372.2	7.5

Table 2. Comparison between the calculated and the measured results of the slag phase

	Al	Ca	Fe	Mg	Mn	K	Na	Si	P
Unit	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%
Measured Data	7.94	25.23	1.22	1.55	0.09	1.21	0.44	15.90	1.92
Calculated Data	8.85	24.02	4.64	1.21	0.08	1.50	0.46	16.63	1.34

Table 3. Calculated composition of the gas phase in Zone I

	H_2O Vol%	N_2 Vol%	H_2 Vol%	CO_2 Vol%	CO Vol%	PN Vol%
Calculated Data	0.17	61.79	1.89	0.73	33.86	0.21

Table 4. Calculated composition of the gas phase in Zone II

	H_2O Vol%	N_2 Vol%	O_2 Vol%	CO_2 Vol%	P_4O_{10} Vol%
Calculated Data	13.45	67.60	2.23	15.38	0.03

Table 5. Calculated composition of the dust in Zone II

	$Na_4P_2O_7$ Mol/min	SiO_2 Mol/min
Calculated Data	0.0045	0.026

Table 6. Comparison between the calculated and the measured results of gas phase in Zone III

	H_2O	N_2 Vol%	O_2 Vol%	CO_2 Vol%	P_4O_{10} Vol%
Calculated Data	12.39	68.47	3.92	13.88	0.027
Measured Data	15.9	68.0	2.9	13.1	

Table 7. Calculated composition of the dust in Zone III

	K g/min	Na g/min	Si g/min	Zn g/min	P g/min
Calculated Data	2.89	0.42	0.74	12.32	0.28