CHAPTER IV

SIMULATION OF A PRIMARY SMELTING REACTOR

In this chapter, the construction of METSIM model for the smelting process of copper concentrate in primary smelting reactor (PSR) was investigated. Emphasis is placed on the determination of an appropriate configuration of the PSR unit which uses the FRL furnace or Teniente converter from pyrometallurgy module in METSIM program to simulate. The model will represent the process accurately by constructing a model through the suitable information such as the sequence of reactions, the extent of reaction, reactor heat loss, product distribution and the mineralogical composition analysis of input materials. Moreover, the important step is to validate the model by comparison of its predictions with actual plant data under the same standard conditions to verify all of the information, for its conceivable uses.

4.1 Building copper smelting process model

Simulation of the primary smelting of copper in a primary smelting reactor (PSR) is carried out using the METSIM program which is widely used in metallurgical process simulation. The FRL furnace simulates an El Teniente converter where the chemistry takes place and heat is generated in the matte phase. This module configuration is shown in Figure 4-1.

From Figure 4-1, the inputs of PSR reactor are dry copper concentrate injected with injection air through 4 tuyeres. Revert, anthracite and flux are fed through the garr gun. Enriched air consists of three sources: first is industrial oxygen which has 95% purity; second is blowing air from the air compressor and the last is annular air which protects tuyeres from wear because of aggressive oxidation reaction. Products of PSR process are white metal, slag and off-gas. Generally, white metal mainly consists of molten sulfide materials or called matte such as Cu_2S and FeS, the principle composition in slag are molten oxide materials for example, fayalite slag (Fe_2SiO_4) and magnetite (Fe_3O_4).

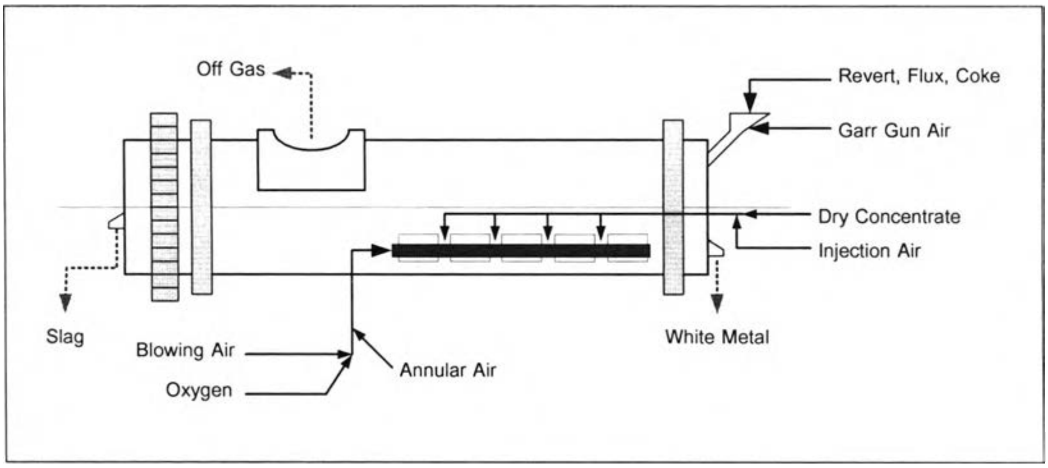

Figure 4-1: Simplify PSR model configuration

The steps involved in building PSR model coupled with a FRL and a MIX unit to represent primary smelting process by using METSIM software are described in Appendix A.

4.1.1 Feed stream characteristics

The METSIM program requires identifying input components with the conditions and phases, which mainly come from copper concentrate, revert, flux and coke in solid phase. Others input are air and industrial oxygen in gas phase.

4.1.1.1 Copper concentrate

The characteristics of copper concentrate are described by physical and chemical properties. Physical properties are similar to general solid particle properties such as size distribution, moisture content, bulk density and others. These are assumed to be constant in the model. On the other hand, chemical properties affect the simulation directly. Generally, the analysis of chemical properties has two different types, the mineralogical and chemical composition. The mineralogical composition defines mineral and other compounds called gangue in concentrate while the chemical composition defines the amount of several elements in concentrate. The mineralogical composition is utilized by inputting in the model and METSIM will calculate chemical composition automatically. The laboratory determines the mineralogical composition by image analysis from optical microscopy equipment. In addition, the mineralogical analysis is more expensive and is more time consuming than chemical analysis, which is determined by X-ray diffraction (XRF) or analyzed by wet chemical methods using reagent grade chemicals and distilled water. In most instances the smelter plant usually determines the chemical analysis and compare with the mineralogical of each type of concentrate.

In this study, three kinds of copper concentrates which are used in actual operation are analyzed and summarized in Table 4-1 and 4-2. The Antamina, Escondida and Collahuasi concentrates are blended together in the specific ratio which came from model simulation so as to get the autogeneous operation. In addition, the image analysis showed that normally copper concentrate contained mainly chalcopyrite, chalcocite, pyrite and gangue. Gangue minerals were mainly silica with other silicates, iron oxides and traces of titanium oxides. All these are associated with the sulphide minerals.

Table 4-1: Chemical composition of Antamina, Escondida and Collahuasi copper concentrates

Composition	Formula	Antamina	Escondida	Collahuasi
Major elements				
Copper	Cu	28.00	36.18	27.43
Iron	Fe	26.00	21.08	26.74
Sulfur	S	33.00	32.77	35.95
Aluminum	Al	0.14	1.59	2.56
Calcium	Ca	0.11	0.08	0.32
Magnesium	Mg	0.10	0.07	0.27
Silicon	Si	0.93	2.80	1.32
Minor elements				
Arsenic	As	0.017	0.14	0.34
Antimony	Sb	0.0155	0.03	0.02
Bismuth	Bi		0.01	0.01
Lead	Pb			0.02
Zinc	Zn		0.15	1.03
Cobalt	Co			
Molybdenum	Mo		0.30	
Gold	Au			0.02

Table 4-2: Mineralogical composition of Antamina, Escondida and Collahuasi copper concentrates

Composition	Formula	Antamina	Escondida	Collahuasi
Mineralogical Composition (%)				
Chalcopyrite	$CuFeS_2$	59.5	9.22	40.82
Chalcosite	Cu_2S	3.5	39.16	5.47
Covellite	CuS	3.5	1.91	9.90
Copper	Cu^{o}		0.05	2.34
Cuprite	CuO		0.06	
Bornite	Cu_5FeS_4	2	0.18	29.11
Pyrrotite	FeS	8		1.79
Pyrite	FeS_2	7.5	38.46	
Enargite	Cu_3AsS_4	0.24	0.37	0.02
Tennantite	$Cu_{12}Sb_4S_{13}$		0.10	1.54
Galena	PbS	0.37		0.03
Blenda or Sphalerite	ZnS	1.66	0.20	0.01
Antimonite	Sb_2S_3			0.02
Bismutite	Bi_2S_3	0.056		
Gold	Au			
Molibdenite	MoS_2		0.50	0.70
Wustite	FeO			
Magnetite	Fe_3O_4			
Hematite	Fe_2O_3		0.48	
Gangue Minerals				
Alumina	Al_2O_3	0.26	3.00	4.84
Calcium oxide	CaO	0.14	0.19	0.14
Magnesium oxide	MgO	0.16	0.11	0.45
Silica	SiO_2	2.00	6.00	2.83

It can be seen from Table 4-2 that the minerals in copper concentrate are mainly chalcopyrite, chalcocite, covellite, bornite, pyrrotite and pyrite. In order to simplify the chemical properties for analysis of process parameters in next chapter, only the important minerals were investigated.

4.1.1.2 Revert

Revert is the by product of copper smelting process, which is generated from many sources such as the accretion of ladle, cleanings from the launders and frozen material ejected from the mouths of PSR and the various other furnaces and slag from Hoboken Siphon Converter and Anode furnace. There are 2 classes of revert materials which were separated by copper grade in the revert yard as high grade revert (>30%Cu) and low grade revert (<30%Cu). The low grade revert are mostly used to recycle in PSR furnace because the high copper content can cause refractory wear and reduce campaign life of the furnace. However, the chemical analysis of revert, which are averaged from daily analysis of actual plant data, is determined to apply the mineralogical composition in the model from the following table:

Table 4-3: Revert composition using in METSIM

Composition	Formula	Revert
Chemical Composition (%)		
Copper	Cu	37.00
Iron	Fe	30.33
Sulfur	S	5.68
Silicon	Si	5.45
Aluminum	Al	1.30
Mineralogical Composition (%)		
Fayalite	Fe_2SiO_4	31.74
Magnetite	Fe_3O_4	17.87
Copper	Cu^o	
Cuprite	Cu_2O	16.42
Chacocite	CuO	
	Cu_2S	28.07
Iron Sulfide	FeS	0.01
Alumina	Al_2O_3	1.36
Silica	SiO_2	0.2

Table 4-3 shows the principal elements and components in revert and the other impurities which come as minor elements in copper ores. Accordingly, there could be several effects of the addition of different revert properties to the primary smelting process because revert consists in fayalite, magnetite and copper oxide.

4.1.1.3 Flux

Silica flux used for slag forming process, is mixed with revert and feed to PSR through garr gun. Flux properties have differences as they come from many sources. In Thailand, most suppliers are in Chonburi and Karnchanaburi province. Normally, the moisture content in silica flux is about 2% and the chemical properties of flux are shown in the following table;

Table 4-4: Properties of silica flux input to METSIM

Composition	Formula	%
Chemical Composition (%)		
Silicon	Si	44.41
Aluminum	Al	2.33
Calcium	Ca	0.26
Magnesium	Mg	0.13
Mineralogical Composition (%)		
Silica	SiO_2	95.00
Alumina	Al_2O_3	4.40
Calcium oxide	CaO	0.36
Magnesium oxide	MgO	0.21

The silica composition was analyzed by x-ray fluorescence instrument and verified by sampling the flux in storage from many position within one lot. The average value is used in the METSIM.

4.1.1.4 Air and oxygen

There are 5 different sources of air supply to PSR furnace depend on their function. First, the injection air is used for conveying and injection of dry copper concentrate through the tuyeres. Secondly, the garr gun air is to apply the force of air pressure to help solid materials go inside the furnace. Thirdly, annular air is air flow in the outside tube of blowing air tuyeres to cool the end of tuyeres line, where the tuyere wear occur from oxidation reaction in furnace. The flow of annular air around the pipeline end will protect the tuyeres. Then, blowing air is supplied in order to dilute high purity of oxygen from 95% to less than 40%. After dilution, the mixed blowing air and oxygen is called enriched air. Finally, industrial oxygen is injected through blowing tuyeres after mixing with blowing air. Oxygen is consumed in the smelting process in pyritic sulfur combustion and slag forming reaction. Table 4-5 shows the standard flow rate of air and oxygen that supply to the PSR furnace which based on design condition where copper concentrate is smelt at 1,700 ton/day.

Table 4-5 Nominal flow rate of air and oxygen supply to PSR

Air and Oxygen Supply	Oxygen Purity (%)	Nominal Flow Rate (Nm^3/hr)
Industrial Oxygen	95	10,002
Blowing Air	21	37,650
Injection Air	21	3,540
Enriched Air	36	51,192
Garr Gun Air	21	3,540
Annular Air	21	Not Design

It is noted that enriched air flow rate is calculated from summation of industrial oxygen, blowing air, injection air and annular air. In additional, the design flow rate may have some differences with actual operation. For example annular air is not stated in nominal value because it was included with enriched air when the plant was designed but was separated after some plant modification. This model was modified to be compatible with the real plant and consider oxygen from enriched air to be reacted in PSR but the garr gun air will not considered because the path of garr gun air is not direct to the molten material in furnace. Consequently, garr gun air in this model will affect only the heat loss through the gas phase.

4.1.2 Process chemistry

Process chemistry of PSR occurs in white metal phase where both of copper concentrate and oxygen injected react inside the bath in the level of matte phase. To calculate the net heat of reaction in PSR, the reactions that transform the feed materials into final product, white metal, slag and off gas, are considered. In addition, the pyritic sulfur reactions which form SO_2 gas from the reaction with O_2 are combined in the first stage that input to the model.

In the following reaction, the two stages of reaction occur.

First stage (Pyritic Sulfur Combustion)			ΔH_{298} (Cal/mole)
$CuFeS_2$ (s) + ½ O_2 (g)	→	½ Cu_2S (s) + FeS (s) + ½ SO_2 (g)	-22,475
FeS_2 (s) + O_2 (g)	→	FeS (s) + SO_2 (g)	-51,350
$2Cu_5FeS_4$ (s) + $1O_2$(g)	→	5 Cu_2S (s) + 2FeS (s) + SO_2 (g)	-15,875
CuS (s) + ½ O_2(g)	→	2 Cu_2S (s) + ½ SO_2	-32,575

The first stage of reaction result in matte production (Cu_2S and FeS) but the calculation of net heat is based on solid phase generation so that it is necessary to input the reaction for changing solid to matte phase as follows;

Cu_2S (s) → Cu_2S (matte)
FeS (s) → FeS (matte)

These two reactions take place over 99.5% of Cu_2S and FeS generate. The rest of them form the copper oxide and magnetite, and when melted, separate to the slag phase as the following reactions;

Reactions						ΔH_{298} (Cal/mole)
Cu_2S (s)	+	$3O_2$ (g)	→	$2Cu_2O$ (s)+	$2SO_2$ (g)	12,345
3FeS (s)	+	$5O_2$ (g)	→	Fe_3O_4 (s) +	$3SO_2$ (g)	12,345

Second Stage (Slag Forming Reaction)			ΔH_{298} (Cal/mole)
FeS (s) + 3/2 O_2 (g)	→	FeO (s) + SO_2 (g)	-115,310
FeO (s) + 1/6 O_2 (g)	→	1/3 Fe_3O_4 (s)	-22,140
FeO (s) + ½ SiO_2 (s)	→	½ Fe_2SiO_4 (s)	-4,800

The main reactions that happen in PSR have two stages. First stage is the decomposition of copper concentrate, which is called pyritic sulfur combustion. The second stage is slag forming reactions.

The heat generated form smelting process depends on the values of the standard enthalpies of reactions of the minerals contained in the concentrate. They are given above. It can be seen that the most exothermic reaction is the oxidation of FeS to FeO, followed by the decomposition of pyrite and covellite. This study will discuss later the variation of mineralogical and elemental composition and their effect on the process variables.

It is noted that, the METSIM program has developed a thermodynamic database of all input components so that the required inputs are the chemical reactions and sequence of these reactions. The mass balance and heat of reaction can be automatically calculated. In additional, all of the reaction and extent of reaction which are inputted in model was shown in Appendix 2.

4.1.3 Process conditions

Teniente Converter Technology is widely used in the copper smelter. The main objective of this technology is to continue autogenous operation with the highest smelting capacity. However, copper smelters can not have the same process conditions and their differences can affect the result of process. It is required therefore to use the model with the same process condition to simulate the process.

It can be seen from Table 4-6 that the controlled operation parameters have been standardized from actual plant data and operate in stable value, some parameters may not have the same values as design and illustrate in Table 4-5.

Table 4-6: Controlled operation parameters in PSR

Parameter	Plant data
White Metal level	1100 mm
Bath level	1600 mm
Blowing air pressure	130 kPa
Injection air flow	2,000 - 4,000 Nm^3/hr
Garr Gun air flow	3,800 - 4,100 Nm^3/hr
Annular air flow	700 - 2,500 Nm^3/hr

It should be noted that model can be simulated with accuracy under this condition. If the controlled operation parameters changed, the inputted parameters in model should be changed. For example, the level of bath has an effect on the extent of reaction in the furnace so that the estimation of model for extent of reaction should be changed. Accordingly, the model can be used to predict the result of operation under this condition.

4.1.4 PSR reactor

The FRL unit, which is representation unit for PSR in this study, is required to apply the appropriate reaction, sequence and extent of reaction, heat loss and phase distribution in the reactor. This module is based on a horizontal cylinder model where the chemistry takes place and heat is generated in the matte phase.

The input parameters for FRL furnace in model are shown in Table 4.5, they can be separately inputted in the Dimensions, Phases and Heat Balance input data screen in METSIM.

It is noted that the molten metal depth is used to calculate the volume of the phases within the furnace. The calculation of the volume of material inside the furnace is related with the heat transfer estimation in the PSR.

Table 4-7: Input parameters of METSIM model

Parameter	FRL furnace in Model
Heat loss	5.1 Mcal/hr
Dimension	. ϕ 4.1 x 21 m (Inside), ϕ 5 x 22 m (Outside)
Depth (m)	White metal 1.1 m, Slag 1.8 m
Phase distribution	
Matte	White metal 87%, PSR Slag 13%
Slag	PSR Slag 100%
Gas	PSR Off gas 99%, White metal 0.5%, PSR Slag 0.5%

4.1.5 Output stream characteristic

The three main product of PSR furnace are consist of white metal and slag which can be take out by opening the tap hole (white metal and slag tap hole). The other product is PSR off gas which contains sulfur dioxide and sends to treat at gas treatment plant. After treating the off gas, the sulfuric acid can be obtained from sulfuric acid plant. In this model, the analysis values of product from actual plant are inputted to find the optimum value of input parameters for the model which are shown in Table 4-6 and 4-7.

According to the design aspects, the Teniente Converter operation is optimized by controlling to 75%copper grade. For process calculations purposes, molten white metal composition considers 75%Cu, 3.9%Fe, 20.8%S and 1%Fe_3O_4. In terms of sulfide components, white metal accounts for 93.92%Cu_2S and 5.08%FeS.

4.2 Estimation of model

In order to find the appropriate value for estimation, the actual plant data set was used and input to the model. With the known results, the configuration of FRL units has change to get the best prediction of model calculation. By comparison with the known results which are %Copper in white metal, %Copper in slag, %magnetite in slag and reactor temperature, the model for this smelter was obtained and validated by another set of actual plant data which was discussed in model validation section.

The variations of input parameters are explained in this section. Table 4-8 shows the input parameters and the result of simulation. All of them can be adjusted by varying the input parameters of the FRL unit which are such as the extent of reaction, reactor temperature and product distribution.

Table 4-8: Comparison of data use for estimation in model and model result

Description	Unit	Plant Data	Result of model
Cu in WM	%	72.43	72.40
WM	ton/hr	530	530.92
Cu in Slag	%	6.02	6.29
Slag	ton	880	884.24
Temperature	celcius	1199.5	1197.15
SO2	%	Not measure	22.18
Fe/SiO2	-	1.473	1.60
Fe3O4	%	18.5	18.18

The operation data that use to estimate the model is shown in Table 4-8. It is verified from operation data that have constant condition and average in one hour.

Table 4-9: Operation data input to estimation of model parameter

Description	Unit	Model Input
Flux	ton/hr	120.40
Revert	ton/hr	196.18
Blowing Air	Nm^3/hr	37,675.57
Oxygen	Nm^3/hr	7,672.31
Calculation		
O2 Efficiency	%	90.47
%Enrichment	%	33

From the data on Table 4-8, the model parameter can be optimized, the following parameters are estimated and use for further study.

4.2.1 Extent of reaction

The operator must know not only the reaction and phases in order to model from METSIM program but also the extent of reaction. This model will calculate mass balance based on the extent of reaction. However, the kinetics of reaction in function of mass flow rate is more complicated and cannot be performed in the model.

4.2.2 Heat loss

The heat loss from the reactor to the surroundings by the common heat transfer mechanisms are related with other factors such as the vessel inside temperature, general reactor geometry and dimensions, size of the gas exhaust mouth, manufacture materials (type of shell steel and refractory brickwork) and others.

According to the heat transfer equations, heat losses have been calculated and obtained an average value of 20 GJ/h from basis of the design calculation. However, the actual heat loss value is different from the design calculation because of the reactor did not operate at the design capacity. The PSR model can be inputted with the reactor dimension and select the automatic heat loss calculation

The value of heat loss is directly affecting the furnace temperature so that in PSR model, it requires further study. The effect of process parameter to the controlled temperature should have the acceptable value of heat loss and this study determines the heat loss by validation with the actual data.

4.2.3 Phase distribution

METSIM carried out mass balance calculations by tracking material flows, which are made up of a mixture of components. These are the chemical species, such as pure chemicals, minerals or elements, and can exist in one or more of eight phases. The phases are identified by their phase number. The phases which are involved in this model are solid inorganic (such as copper concentrate, flux), solid organic which is anthracite, liquid (such as water), molten sulfides (white metal), molten oxides (slag) and gas such as sulfur dioxide, oxygen, nitrogen.

In actual operation, the extraction of slag always have white metal contaminated with the slag so that the electric furnace is required to recover copper loss which are white metal and copper entrapped in PSR slag.

The plant data that used for estimation of the model is shown in Table 4-8. The inputted parameters of FRL unit which are phase distribution and heat loss are adjusted by trial and error until the results are near the actual data. However, the extent of reaction can be calculated by the function in METSIM program.

4.3 Model validation

In order to use the model from METSIM for simulating a primary smelting reactor unit with confidence, the reliability of the model is tested by comparing the simulated results obtained on this study with the operating data from plant on February 2007. With the same standard operating conditions from Table 4-5 in this paper, the results of the simulation run in comparison to the operating data are shown in Figure 4-2 through Figure 4-5. It can be seen that the compositions in the white metal and magnetite content in PSR slag and temperature in furnace as calculated by METSIM are in good agreement with the operating data except of %Cu in slag.

4.3.1 Operation data

The operation data is selected from the same standard conditions as the model. This is shown in Table 4-9.

Table 4-10: Data input for simulation in program and comparison with actual plant data

INPUT	UNIT	Data 1	Data 2	Data 3	Data 4	Data 5	Data 6	Data 7	Data 8	Data 9	Data 10
Dry Concentrate	tpd	1,565	1,567	1,555	1,540	1,537	1,525	1,565	1,493	1,482	1,481
Flux	tpd	120	119	120	120	121	120	120	119	121	121
Revert	tpd	239	240	240	240	240	240	228	120	192	192
Blowing Air	Nm^3/hr	36,584	36,745	37,854	37,912	37,948	37,881	37,870	37,931	36,469	36,295
Oxygen	Nm^3/hr	7,500	7,865	7,867	7,886	7,889	7,860	7,883	7,169	7,099	7,035
O_2 Coefficient	Nm^3/ton	242	247	250	253	253	254	248	249	249	248
%Enrichment	%	32.9%	33.4%	33.3%	33.4%	33.4%	33.3%	33.4%	32.4%	32.4%	32.3%
Garr Gun Air	Nm^3/hr	4,006	3,996	4,007	3,997	3,999	4,003	3,997	4,000	4,004	4,013
Injection Air	Nm^3/hr	1,816	1,832	1,947	1,909	1,903	1,878	1,917	1,790	1,840	1,869

4.3.2 Validation result

The validation results can be illustrated in Figure 4-2 through Figure 4-5 which were compared between actual plant data and simulation data in %Cu in white metal, %Cu in PSR slag, %Fe_3O_4 in PSR slag and temperature of furnace. It can be seen that the %Cu in PSR slag is slightly different with actual plant data.

The difference in results of %Cu in slag can be described by the way sampling of slag is done. Different operators take samples on different time and position. To reduce the error from different person, the taking of slag sampling and work instruction has been prepared. However, the schedule of tapping can also affects this data due to phase level in the furnace.

In conclusion, the operating data that compiles with the model need to have the same standard conditions especially related with the efficiency of oxygen so that the use of model should be under the same condition of bath level, air supply flow rate and pressure to get more accuracy. However, consistency of slag sampling is also required for comparison of the copper in slag data.

From this operational set of parameter, the calculation of oxygen efficiency is about 91% from actual plant data. The typical value is about 95% (Lurachi and Canas, 1997). The white metal and bath level illustrate the level variation which are not included in the model and assumed to be constant for steady state operation. However, in real production schedule it is hard to maintain constant bath level. The other controlled parameters can be controlled close to the design criteria of the furnace.

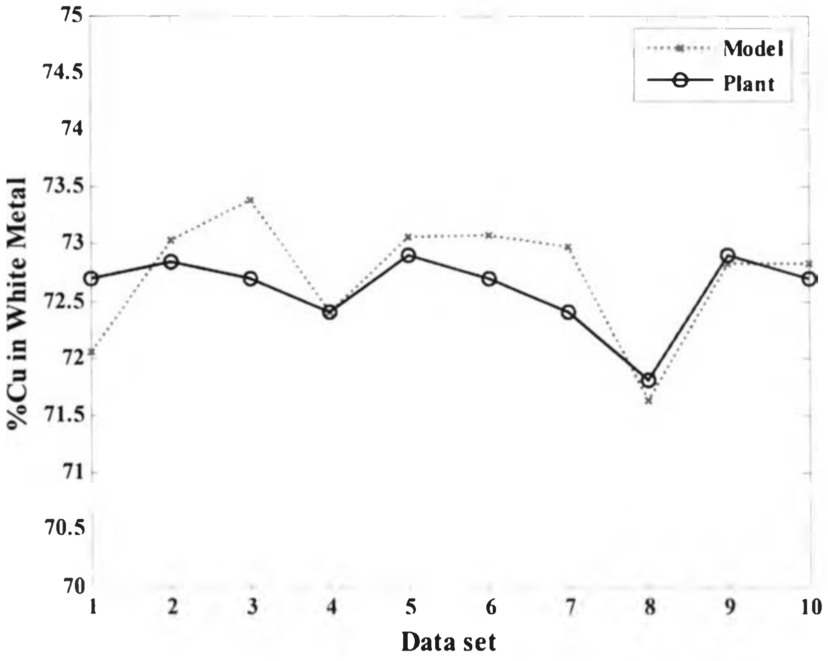

Figure 4-2: Comparison of %Cu in White metal from simulated results and operating data

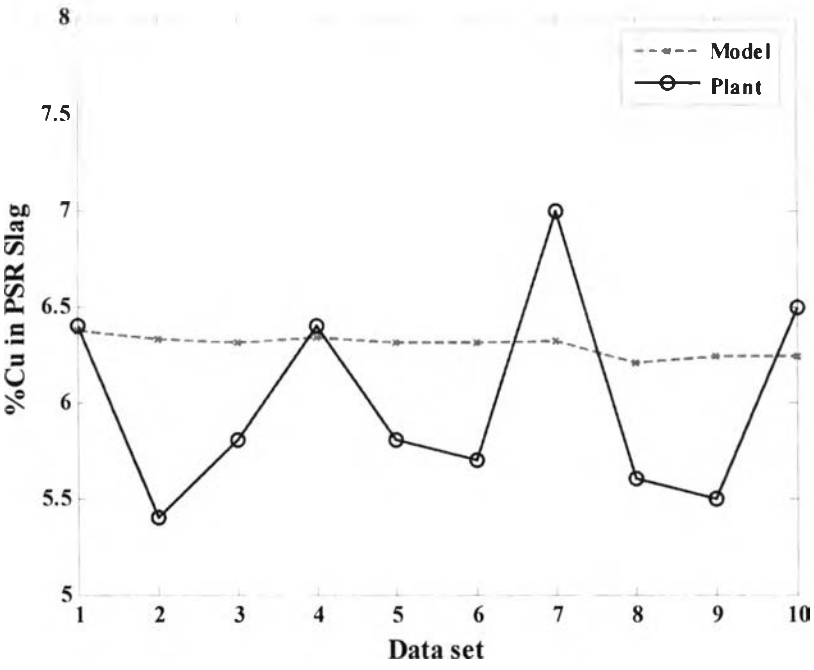

Figure 4-3: Comparison of %Cu in slag from simulated results and operating data

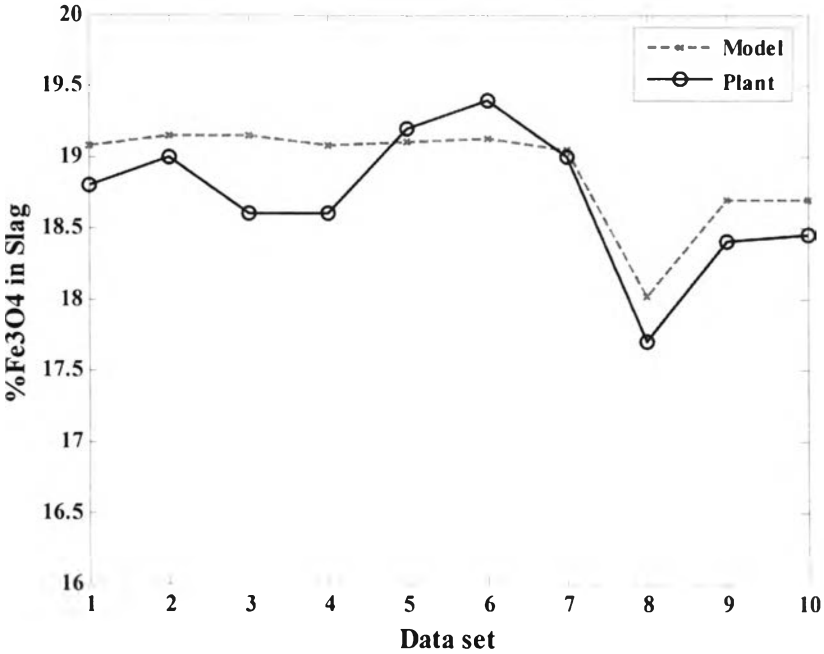

Figure 4-4: Comparison of $\%Fe_3O_4$ in slag from simulated results and operating data

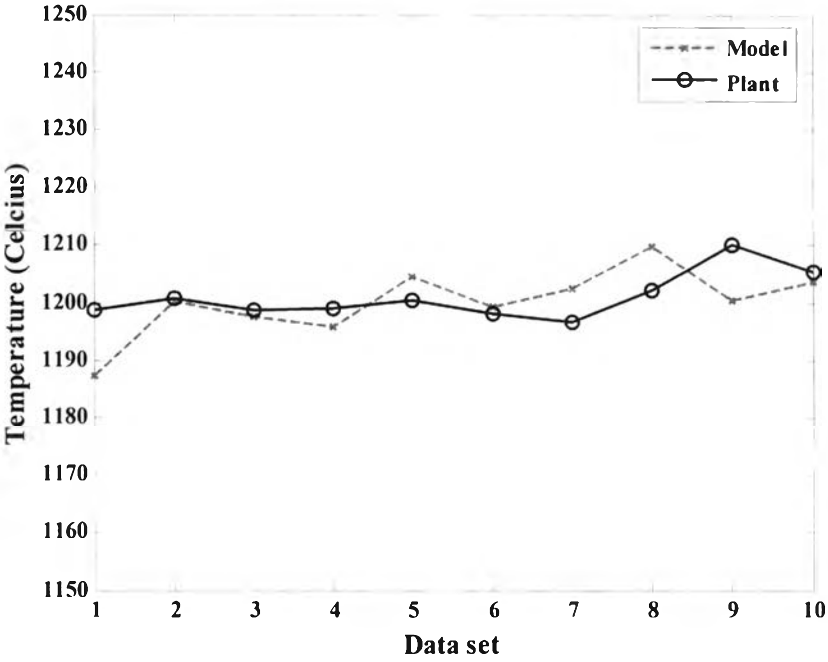

Figure 4-5: Comparison of temperature in furnace from simulated results and operating data