APPENDIX - A

CALCULATION OF INLET GAS COMPOSITION

The inlet gas composition is a mixture of CO,CO_2 and SO_2 in different proportions to obtain the required oxygen and sulphur potentials a t 1523K .

The species considered are CO,CO_2 ,SO_2 , S_2 ,O_2. The reactions and equilibrium constants at 1523K are listed below:

$$CO_2 = CO + 0.5\ O_2$$

$$0.5S_2 + O_2 = SO_2$$

The equilibrium constants were calculated with FACTSAGE.

Another reaction considered in the calculation is

$$Fe + 0.5\ O_2 = FeO$$

due to the influence of iron in the system.

$$Fe_l + 0.5\ O_2 = FeO_l \qquad k_1 = 4.95\text{x}10^5 \qquad (1)$$

$$CO_2 = CO + 0.5\ O_2 \qquad k_2 = 7.23\text{x}10^{-6} \qquad (2)$$

$$0.5\ S_2 + O_2 = SO_2 \qquad k_3 = 6.9\text{x}10^9 \qquad (3)$$

From equations (1) to (3) written above, we write:

$$k_1 = \frac{a_{FeO}}{a_{Fe} \cdot p_{O_2}^{0.5}} \qquad (4)$$

$$k_2 = \frac{p_{CO} \cdot p_{O_2}^{0.5}}{p_{CO_2}} \qquad (5)$$

$$k_3 = \frac{p_{SO_2}}{p_{S_2}^{0.5} \cdot p_{O_2}} \qquad (6)$$

$$p_T = p_{S2} + p_{CO} + p_{CO2} + p_{O2} + p_{SO2} \qquad (7)$$

If $$x = \frac{p_{CO_2}}{p_{CO}} \quad (8)$$

Combining (5) and (8),

$$x = \frac{p_{O_2}^{0.5}}{k_2} \quad (9)$$

From equation (6),

$$p_{SO_2} = (k_3).p_{O_2}.(p_{S_2})^{0.5} \quad (10)$$

Results

a_{FeO}	a_{Fe}	p_{O2}	p_{CO}/p_{CO2}	a_s	$\mathbf{p_{SO2}}$	$\mathbf{p_{CO2}}$	$\mathbf{p_{CO}}$	Total gas	$\%SO_2$	$\%CO_2$	%CO
0.37	6.05E-03	1.53E-08	5.85E-02	<<0	0.44	0.45	0.02	0.91	48.07	49.24	2.68
0.37	5.55E-03	1.81E-08	5.37E-02	<<0	0.51	0.37	0.02	0.90	56.55	41.39	2.07
0.37	5.03E-03	2.21E-08	4.87E-02	<<0	0.61	0.27	0.01	0.90	68.21	30.42	1.37
0.37	4.49E-03	2.78E-08	4.34E-02	<<0	0.76	0.13	0.01	0.90	84.99	14.43	0.58

The total pressure used in the calculation is 0.86 atmospheres, average pressure in Pretoria and a_{Fe} was obtained with FactSage calculation.

APPENDIX-B.

MATTE, SLAG AND ALLOY COMPOSITION

B.1. Matte, slag and gas starting composition

A total of four series were conducted, comprising of 21 experiments in the following conditions:

T: 1523 K

Flowing gas: CO,CO_2,SO_2

Table B-1 presents the starting charge composition of the matte and slag used in the first series of experiments. A total of four sub-series were conducted comprising three experiments for each sub-series.

Matte	Wt%Fe	Wt%Cu	Wt%Ni	Wt%S
Test 1	8.8	19.9	49.7	21.2
Test 2	7.6	21.2	54.8	16.4
Test 3	5.3	27.3	50.4	17.0
Test 4	4.0	23.9	50.3	21.8

Slag	Wt%Fe	Wt%Si	Wt%O
All	54.8	16.3	28.9

Table B-1. Starting charge composition for different experimental series.

Table B-2 presents the expected oxygen pressures for the various experimental tests. The oxygen activity increases for each test while the sulphur activity decrease. These results have been obtained using the FACTSAGE and the quasichemical calculation [PISTORIUS]. The log P_{O2} varied from –7.82 to –7.56 and the log P_{S2} varied from –2.38 to –2.40.

Test	PS_2(atm)	PO_2(atm)
1	4.15×10^{-3}	1.53×10^{-8}
2	4.09×10^{-3}	1.81×10^{-8}
3	4.04×10^{-3}	2.21×10^{-8}
4	3.98×10^{-3}	2.78×10^{-8}

Table B-2.Oxygen and Sulphur pressures for the various experimental series.

Table B-3 shows the inlet gas composition required to yield the desired oxygen and sulphur pressures for different experiments at 1250°C.

Log pO_2	p $_{SO_2}$	p $_{CO_2}$	p $_{CO}$
-7.82	0.44	0.45	0.02
-7.74	0.51	0.37	0.02
-7.66	0.51	0.27	0.01
-7.56	0.76	0.13	0.01

Table B-3. Inlet gas composition

Table B-3' below presents the matte composition obtained with two different gas mixture composition. Composition with * was obtained with Ar gas .

		*		*		*		*
	Wt% Fe		**Wt% Cu**		**Wt% Ni**		**Wt% S**	
	8.3	8.3	25.1	24.9	46.1	46.2	20.4	20.6
	8.2	8.7	29.4	24.9	42.6	44.8	20	21.5
	8.8	8.3	24.8	28.9	45.1	42.4	21.4	20.3
Average	8.4	8.4	26.4	26.2	44.6	44.5	20.6	20.8
Standard deviation	0.3	0.2	2.6	2.3	1.8	1.9	0.7	0.6
95% confidence interval	0.8	0.7	6.4	6.1	4.5	4.6	1.8	1.7

Table B-3'. Results of composition obtained with different gas composition

B.2.Tests run using Cr/Cr_2O_3 reference electrode.

Table B-4 presents the results of the composition before and after different tests. The samples were analysed especially for iron content in the different phases. The scanning electronic microscope was used in that purpose, in SE mode.

	Test 1			
	Wt%Fe	**Wt%Cu**	**Wt%Ni**	**Wt%S**
	8.3	25.1	46.1	20.4
	8.2	29.4	42.6	20
	8.8	24.8	45.1	21.4
average	8.4	26.4	44.6	20.6
Standard Deviation	0.3	2.6	1.8	0.7
95%confidence interval	0.8	6.4	4.5	1.8

	Test 2			
	Wt%Fe	**Wt%Cu**	**Wt%Ni**	**Wt%S**
	3.9	27.3	50.4	18.4
	4.2	24.1	51	20.2
	4.6	25.3	47.5	23.4
Average	4.2	25.6	49.6	20.7
Standard Deviation	0.4	1.6	1.9	2.5
95%confidence interval	0.9	4.0	4.6	6.3

	Test 3			
	Wt%Fe	**Wt%Cu**	**Wt%Ni**	**Wt%S**
	2.2	25.5	54.4	16.8
	2.2	28.5	52.5	16.8
	2.2	28.5	54.4	14.7
average	2.2	27.5	53.8	16.1
Standard Deviation	0.0	1.7	1.1	1.2
95%confidence interval	0.0	4.3	2.7	3.0

	Test 4			
	Wt%Fe	**Wt%Cu**	**Wt%Ni**	**Wt%S**
	1.3	26.7	51.7	20.4
	1.2	22.6	54.8	21.1
	1.3	24.7	53.2	20.8
average	1.3	24.7	53.2	20.8
Standard Deviation	0.1	2.1	1.6	0.4
95%confidence interval	0.1	5.1	3.9	0.9

Cr_2O_3 slag

	Test 1	
	Wt%Fe	**Wt%Si**
	77	23
	79.9	20.1
	78.3	21.7
average	78.4	21.6
Standard Deviation	1.5	1.5
95%confidence interval	3.6	3.6

	Test 2	
	Wt%Fe	**Wt%Si**
	78.6	21.4
	81.9	18.9
	80.5	19.5
average	80.3	19.9
Standard Deviation	1.7	1.3
95%confidence interval	4.1	3.2

	Test 3	
	Wt%Fe	**Wt%Si**
	84.9	15.1
	84.4	15.6
	83.3	16.7
average	84.2	15.8
Standard Deviation	0.8	0.8
95%confidence interval	2.0	2.0

	Test 4	
	Wt%Fe	**Wt%Si**
	80.9	19.1
	81.6	18.4
	79.6	20.4
average	80.7	19.3
standevia	1.0	1.0
confidence	2.5	2.5

Table B-4. Results of different experimental tests.

B.3. Tests run with Fe/FeO reference electrode

B.3.1. FeO-SiO_2 slag

The results show below has been proceed in an argon atmosphere in the following conditions:

T: 1523 K

Flowing gas: N_2

The table B-5 shows the results obtained

	Test 1			
	Wt% Fe	**Wt% Cu**	**Wt% Ni**	**Wt% S**
	7	21.2	48.5	22.9
	7.6	24.1	45.9	22.5
	5	25.1	47.4	22.1
	7.7	24	50.9	17.3
	5.5	20	52.1	22.4
	5.6	21.2	52.4	20.8
	6.3	24.1	44.9	24.7
average	6.4	22.8	48.9	21.8
Standard Deviation	1.1	2.0	3.0	2.3
95%confidence interval	1.0	1.8	2.8	2.1

	Test 2			
	Wt% Fe	**Wt% Cu**	**Wt% Ni**	**Wt% S**
	7	22.1	50.4	21.3
	6.1	22.5	50.8	21.3
	4.5	20	50.4	25.3
	8	19.6	49.6	22.9
	6.3	24.2	48.2	21.4
	5.4	25.8	50.3	18.5
	5.5	23.5	50.3	20.6
	4.9	18.6	55.2	20.3
average	6.0	22.5	50.7	21.5
Standard Deviation	1.1	2.5	2.0	2.0
95%confidence interval	1.0	2.1	1.7	1.7

	Test 3			
	Wt% Fe	**Wt% Cu**	**Wt% Ni**	**Wt% S**
	4.2	24.1	51	20.2
	2.1	19.9	54.6	23.3
	5.2	20.9	50.4	23.1
	4.8	22.9	53.1	19.2
	3	18.4	58.1	20.5
	3.8	23.3	53.1	19.8
	2.7	20.8	49.1	27.4
average	3.7	21.5	52.8	21.9
Standard Deviation	1.14	2.04	3.01	2.89
95%confidence interval	1.05	1.89	2.78	2.68

	Test 4			
	Wt% Fe	**Wt% Cu**	**Wt% Ni**	**Wt% S**
	2.4	22.6	54.8	20.3
	2.1	23.6	54.4	19.9
	3.5	25.3	50.1	21.1
	2.4	19	49.5	29.1
	3.6	23.3	52.1	20.9
	2.7	26.3	46.5	24.4
	2.8	19.5	56.6	21.1
average	2.8	22.8	52.0	22.4
Standard Deviation	0.6	2.7	3.5	3.3
95%confidence interval	0.5	2.5	3.3	3.0

	Test 5			
	Wt% Fe	**Wt% Cu**	**Wt% Ni**	**Wt% S**
	2.1	27.8	50.4	19.7
	2	27.2	50.8	20.1
	2.1	22.6	51.7	23.6
	2.4	23.2	51	23.4
	2.4	19.7	56.1	21.7
	2.3	20.4	53	24.3
average	2.2	23.5	52.2	22.1
Standard Deviation	0.2	3.4	2.1	1.9
95%confidence interval	0.2	3.5	2.2	2.0

	Test 6			
	Wt% Fe	**Wt% Cu**	**Wt% Ni**	**Wt% S**
	0.7	20.8	53	25.5
	0.9	23.7	50.7	24.7
	0.5	23.7	51.6	24.2
	0.9	23.1	49.5	26.5
	0.4	18.4	50.1	31.1
	0.7	27.7	51.5	20.1
average	0.7	22.9	51.1	25.4
Standard Deviation	0.2	3.1	1.2	3.6
95%confidence interval	0.2	3.3	1.3	3.7

	FeO slag	
	Test 1	
	Wt%Fe	**Wt%Si**
	81.6	18.4
	82.1	17.9
	78.8	21.2
average	80.8	19.2
Standard Deviation	1.8	1.8
95%confidence interval	4.4	4.4

	Test 2	
	Wt%Fe	**Wt%Si**
	81.4	18.6
	79.3	20.7
	79.6	20.4
average	80.1	19.9
Standard Deviation	1.1	1.1
95%confidence interval	2.8	2.8

	Test 3	
	Wt%Fe	**Wt%Si**
	80.2	19.8
	80.4	19.6
	80.1	19.9
average	80.2	19.8
Standard Deviation	0.2	0.2
95%confidence interval	0.4	0.4

	Test 4	
	Wt%Fe	**Wt%Si**
	82	18
	80.6	19.4
	80.5	19.5
average	81.0	19.0
Standard Deviation	0.8	0.8
95%confidence interval	2.1	2.1

	Test 5	
	Wt%Fe	**Wt%Si**
	80.4	19.6
	82.5	17.5
	81.1	18.9
average	81.3	18.7
Standard Deviation	1.1	1.1
95%confidence interval	2.7	2.7

	Test 6	
	Wt%Fe	**Wt%Si**
	80.6	19.4
	81.2	18.8
	78.7	21.3
average	80.2	19.8
Standard Deviation	1.3	1.3
95%confidence interval	3.2	3.2

Table B-5. Composition of different experimental tests (FeO/SiO_2 slag).

All the EMF values shown below are EMF_{cell} .

$E_{cell} = E_{meas} - E_{Fe\text{-}Pt}$

$= E_{meas} - 0.017$ V

Test1		**Test 2**		**Test 3**	
EMF (mV)	**log pO2(atm)**	**EMF (mV)**	**log pO2(atm)**	**EMF (mV)**	**log pO2(atm)**
-161	-9.2	-181	-8.93	-184	-8.89
-154	-9.29	-177	-8.99	-187	-8.85
-151	-9.33	-176	-9.00	-189	-8.83
-148	-9.37	-174	-9.03	-194	-8.76

Test4		Test 5		Test 6	
EMF (mV)	log pO2(atm)	EMF (mV)	log pO2(atm)	EMF (mV)	log pO2(atm)
-218	-8.44	-226	-8.34	-229	-8.3
-212	-8.52	-220	-8.42	-226	-8.34
-211	-8.54	-216	-8.47	-221	-8.4
-208	-8.58	-214	-8.50	-218	-8.44

Table B-6. EMF results obtained with FeO-SiO_2 slag

B.3.2. FeO-Fe_2O_3-SiO_2 slag

The results show below has been proceed in an argon atmosphere in the following conditions:

T: 1523 K

Flowing gas: N_2

The table B-8 below shows the results of the experiments

	Test 1			
	Wt% Fe	Wt% Cu	Wt% Ni	Wt% S
	6.9	22.8	50.4	20
	5.6	25.1	50.4	18.9
	6.5	24.6	45.4	23.5
	5.6	25	45.4	24
	6.6	26.5	47.5	19.4
	6.8	22.6	51.5	19
	6.9	16.7	50.1	26.4
	6.6	26.5	47.9	19.1
Average	6.4	23.7	48.6	21.3
Standard Deviation	0.5	3.2	2.4	2.9
95%confidence interval	0.4	2.7	2.0	2.4

	Test 2			
	Wt% Fe	Wt% Cu	Wt% Ni	Wt% S
	5.4	28.3	45.7	20.7
	4.1	25.6	46.5	23.9
	5.5	26.6	47.6	20.6
	4.9	18.6	55.2	20.3
	4.9	23.1	50.6	21.3
	5.4	27.6	46.5	20.5
average	5.0	25.0	48.7	21.2
Standard Deviation	0.5	3.6	3.6	1.4
95%confidence interval	0.6	3.8	3.8	1.4

	Test 3			
	Wt% Fe	**Wt% Cu**	**Wt% Ni**	**Wt% S**
	3.8	18.2	55.1	22.9
	3.8	17.4	52.9	25.9
	4.2	18.6	52	25.2
	4.2	22.7	50.9	22.2
	4	27.3	47.2	21.5
	3.2	25.2	50.1	21.5
	3.5	27.6	47	21.9
average	3.8	22.4	50.7	23.0
Standard Deviation	0.4	4.4	3.0	1.8
95%confidence interval	0.3	4.1	2.7	1.7

	Test 4			
	Wt% Fe	**Wt% Cu**	**Wt% Ni**	**Wt% S**
	2.4	22.6	53.8	21.3
	2.9	22.6	51.8	22.7
	2.2	19.4	49.2	29.2
	2.4	19.9	56	21.7
	3.1	19.8	55.9	21.2
	2.6	25	50.8	21.8
average	2.6	21.6	52.9	23.0
Standard Deviation	0.3	2.2	2.8	3.1
95%confidence interval	0.4	2.3	2.9	3.2

	Test 5			
	Wt% Fe	**Wt% Cu**	**Wt% Ni**	**Wt% S**
	1.1	30.1	47	21.9
	0.5	26.7	46.1	26.7
	0.9	20	52.1	27
	0.5	16.3	52.8	30.4
	1	17.9	50.1	31
	0.7	31	48.2	20.1
	0.8	29.2	48.6	21.2
average	0.8	24.5	49.3	25.5
Standard Deviation	0.2	6.2	2.5	4.4
95%confidence interval	0.2	5.7	2.3	4.1

	Test 1	
	Wt%Fe	**Wt%Si**
	67.8	32.2
	64.8	35.2
	68.1	31.9
average	66.9	33.1
Standard Deviation	1.8	1.8
95%confidence interval	4.5	4.5

	Test 2	
	Wt%Fe	**Wt%Si**
	69.6	30.4
	68	32
	67.2	32.8
average	68.3	31.7
Standard Deviation	1.2	1.2
95%confidence interval	3.0	3.0

	Test 3	
	Wt%Fe	**Wt%Si**
	67	33
	66.2	33.8
	67.8	32.2
average	67.0	33.0
Standard Deviation	0.8	0.8
95%confidence interval	2.0	2.0

	Test 4	
	Wt%Fe	**Wt%Si**
	67.4	32.6
	66.9	33.1
	66.2	33.8
average	66.8	33.2
Standard Deviation	0.6	0.6
95%confidence interval	1.5	1.5

	Test 5	
	Wt%Fe	**Wt%Si**
	67.8	32.2
	67.9	32.1
	67	33
average	67.6	32.4
Standard Deviation	0.5	0.5
95%confidence interval	1.2	1.2

Table B-7. Composition of different experimental tests ($FeO/Fe_2O_3/SiO_2$ slag).

Test1		**Test 2**		**Test 3**	
EMF (mV)	**log pO2(atm)**	**EMF (mV)**	**log pO2(atm)**	**EMF (mV)**	**log pO2(atm)**
-161	-9.2	-215	-8.48	-230	-8.28
-162	-9.18	-207	-8.59	-229	-8.30
-169	-9.09	-206	-8.60	-213	-8.51
-186	-8.87	-196	-8.73	-201	-8.67

Test4		**Test 5**	
EMF (mV)	**log pO2(atm)**	**EMF (mV)**	**log pO2(atm)**
-204	-8.63	-233	-8.24
-210	-8.55	-232	-8.26
-232	-8.26	-216	-8.47
-234	-8.23	-212	-8.52

Table B-8. EMF results obtained with $FeO-Fe_2O_3-SiO_2$ slag

B.4. Alloy composition

Tests with FeO slag

Test 1

Platinum	40.3	2.9
Nickel	25.6	75.6
Copper	4.1	11.0
Iron	13.2	10.5

Test 2

iron	13.5	13.7	4.2	9.6	1.5
nickel	72.2	78.5	80	82.3	75.8
copper	14.2	7.8	15.8	8.1	22.7

Test 3

Iron	38.3	56.8
copper	29.1	43.2

Test 3

nickel	64.2
Copper	35.8

Test 4

iron	94.7	98.3
nickel	5.3	1.7

Tests with FeO+ Fe_2O_3 slag

Test 1

Platinum	45.6	34.1
Nickel	34.4	46.6
Copper	9.6	7.4
Iron	10.4	11.9

Test 2

iron	1.6	11.2	11.7	12
nickel	78.9	80.7	80.5	80.5
copper	19.5	8	7.8	7.5

Test 3

nickel	58	15
Copper	42	85

APPENDIX-C.

DISCUSSION ON EQUILIBRIUM IN COMPLEX SYSTEMS

C.1. The phase rule for reactive component [RAO, 1985:69]

Consider a heterogeneous system composed of N chemical species or constituents. Except in simple systems, the number of species is different from the number of components. For simplicity, assume that only three of the N species are chemically active and participate in the following reaction:

$$AB_{(s)} = A_{(g)} + B_{(g)}.$$

The number of variables is found in the same manner as with no reactive species.

Thus, total number of variables = p(N –1) + 2 (1)

Where p: number of phases and N: number of species

Phase-equilibrium considerations provide a total of n (p-1) equations. These enable us to fix n(p-1) variables.

The fact that the independent reaction equilibrium $AB_{(s)} \rightarrow A_{(g)} + B_{(g)}$ exists provides the following additional equation. For the reaction at equilibrium,

$\Delta G = 0 = \mu_A + \mu_B - \mu_{AB}$ (2)

Additionally, in the absence of $A_{(g)}$ and $B_{(g)}$ in the starting reacting mixture, stoichiometric considerations require that $p_A = p_B$ (3)

Sometimes special restrictions are placed on the system. For instance, suppose that in the system under consideration the partial pressure of A is fixed at, say, λ atm. This gives the following additional equation:

$$P_A = \lambda$$

We found by summation that

Total number of equations = n (p-1) +1+1+1 (4)

The variance or the number of degrees of freedom is found by subtracting equation (4) from (1).

Thus, F= p (N-1) +2 – N (p-1) –3 = (N-2) –p+1 = c-p+1

Where c is the number of components.

Generalizing, for a system in which there are r independent chemical equilibria, s stoechiometric relations (or constraints), and t special constraints, we have
F = (N-r-s-t) – p +2 = c-p+2-t
Where, in complex systems, the number of components is given by C = N- r- s

Atom matrix is a numerical schemes used in computational mathematics to determine the elemental (or atom) coefficient of an element or species and the minimum number of independent reactions describing the chemical system.

In a closed system, suppose that there are N species that in principle can be synthesized from M elements. Let A_i denote the *i*th species and e_j represent the *j*th element (or atoms of the *j*th kind). Then in matrix notation, we can write

$$A_i = \sum_{j=1}^{M} a_{ij} e_j \quad (i = 1,2\ldots N)$$

Where a_{ij} is the elemental (or atom) coefficient that denotes the number of atoms of the *j*th element present in one molecule of the *i*th species. The rank of an atom matrix is a useful quantity for determining the minimum number of independent reactions required to describe the chemical system.

Applying the above theory to the complex system Fe-Ni-Cu-S-Si-O-C of synthetic matte and slag used in this thesis mentioning that the advantage of using synthetic matte and slag avoid to affect the quality of the final products with minor elements between matte, slag and gas.

A matte: Cu-Fe-Ni-S
A slag: Fe-O-Si; excess of SiO_2
The inlet gas composed of CO-CO_2-SO_2 mixed to obtain the required oxygen and sulphur partial pressure at 1250°C.
At equilibrium, the system has twelve species: $Cu_2S_{(s)}$, $Cu_2O_{(s)}$, $FeS_{(s)}$, $FeO_{(s)}$, $Ni_3S_{2(s)}$, $NiO_{(s)}$, $SiO_{2(s)}$, CO, CO_2, SO_2, S_2, O_2.

C.1.1.Atom matrix

The matrix of atom coefficients is deduced as follows:

I	Species	C(j=1)	O(j=2)	S(j=3)	Fe(j=4)	Cu(j=5)	Ni(j=6)	Si(j=7)
1	CO	1	1	0	0	0	0	0
2	CO_2	1	2	0	0	0	0	0
3	SO_2	0	2	1	0	0	0	0
4	S_2	0	0	2	0	0	0	0
5	O_2	0	2	0	0	0	0	0
6	FeS	0	0	1	1	0	0	0
7	FeO	0	1	0	1	0	0	0
8	Ni_3S_2	0	0	2	0	0	3	0
9	NiO	0	1	0	0	0	1	0
10	Cu_2S	0	0	1	0	2	0	0
11	Cu_2O	0	1	0	0	2	0	0
12	SiO_2	0	2	0	0	0	0	1

Atom matrix can be used to determine the minimum number of independent reactions describing the chemical system.

$$\begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 2 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 0 & 3 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 2 & 0 & 0 \\ 0 & 1 & 0 & 0 & 2 & 0 & 0 \\ 0 & 2 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

The rank of this matrix is found by reducing it to echelon form by a series of row operations. The resultant echelon matrix is

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} ; \text{Rank} = 7$$

This means that seven species among twelve are required to synthesize the total system. The seven species select are CO,CO_2 ,SO_2 ,FeS , Cu_2S ,Ni_3S_2 and SiO_2. The rank of the atom matrix determines the minimum number of independent reactions, in this case seven, required to describe the system.

C.1.2. Number of independent reactions in a chemical system [RAO, 1985:67] can be determined by the rank of stoichiometric coefficient matrix.

In the system composed of N species, there occur several reactions, involving some or all of the species present. Suppose that R is the number of possible reactions, not all of which can be linearly independent. Conversion of reactants to products can be written as follows:

$$\Sigma \nu_{ki} \overset{N}{\underset{i=1}{A_i}} = 0 \, (k = 1,2,\ldots,\mathrm{R})$$

where ν_{ki} is the stoichiometric coefficient of the *i*th species in the *k*th reaction.

An R x N stoichiometric coefficient matrix for the system can be construct where each row vector in this matrix represents a possible reaction.

The linearly independent reactions are determined by the rank of the matrix.

Consider the Fe-Cu-Ni-Si-C-O-S system used in the thesis, twelve species are present: $Cu_2S_{(s)}$, $Cu_2O_{(s)}$, $FeS_{(s)}$, $FeO_{(s)}$, $Ni_3S_{2(s)}$, $NiO_{(s)}$, $SiO_{2(s)}$, CO, CO_2, SO_2, S_2, O_2.

The possible reactions can be written between these species:

$CO + ½ O_2 = CO_2$

$FeS + 3/2 O_2 = FeO + SO_2$

$Cu_2S + 3/2O_2 = Cu_2O + SO_2$

$Ni_3S_2 +7/2 O_2 = 3NiO + 2SO_2$

$FeS + NiO = FeO + Ni_3S_2$

$Cu_2S + FeO = Cu_2O + FeS$

$FeS + 3/2 O_2 = FeO + SO_2$

$½ S_2 + O_2 = SO_2$

$2FeO + SiO_2 = 2FeO.SiO_2$

$Ni_3S_2 + O_2 = NiO + SO_2$

$CO + FeO + SO_2 = CO_2 + FeS + O_2$

These equations rewrite are

$CO + ½ O_2 - CO_2 = 0$

$FeS + 3/2 O_2 - FeO - SO_2 = 0$

$Cu_2S + 3/2O_2 - Cu_2O - SO_2 = 0$

$Ni_3S_2 +7/2 O_2 - 3NiO - 2SO_2 = 0$

$FeS + 3NiO + S_2 - FeO - Ni_3S_2 - SO_2 = 0$

$Cu_2S + FeO - Cu_2O - FeS = 0$

$½ S_2 + O_2 - SO_2 = 0$

$2FeO + SiO_2 - 2FeO.SiO_2 = 0$

$CO + FeO + SO_2 - CO_2 - FeS - O_2 = 0$

The stoichiometric-coefficient matrix is given by

CO	CO_2	SO_2	S_2	O_2	FeS	FeO	Cu_2S	Cu_2O	Ni_3S_2	NiO	SiO_2	Fe_2SiO_4
1	-1	0	0	½	0	0	0	0	0	0	0	0
0	0	-1	0	3/2	1	-1	0	0	0	0	0	0
0	0	-1	0	3/2	0	0	1	-1	0	0	0	0
0	0	-2	0	7/2	0	0	0	0	1	-3	0	0
0	0	-1	1	0	1	-1	0	0	-1	3	0	0
0	0	0	0	0	-1	1	1	-1	0	0	0	0
0	0	-1	1/2	1	0	0	0	0	0	0	0	0
0	0	0	0	0	0	2	0	0	0	0	1	1
1	-1	1	0	-1	-1	1	0	0	0	0	0	0

The rank of the matrix is six obtained using an echelon matrix.

$$
\begin{bmatrix}
1 & -1 & 0 & 0 & 0 & 0 & 0 & 2 & -2 & -1 & 3 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & -7 & 7 & 3 & -9 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & -6 & 6 & 2 & -6 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & -4 & 4 & 2 & -6 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & -1 & 1 & 0 & 0 & 0.5 & 0.5 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0.5 & 0.5 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{bmatrix}
$$

That means there are six independent reactions in this system.

APPENDIX - D

FURNACE ASSEMBLY COMPONENTS

			Dimensions		
Part	**Materials**	**Supplier**	I.D. (cm)	O.D. (cm)	Lt (cm)
Crucible	Silica	Lenton	4.3	4.5	3.9
Furnace tube	Mullite	C.C. Imelmann	6.4	7.3	52
Gas inlet tube	Silica	Lenton	4	6	48
Sampling tube	Silica	Lenton	4	6	60
Thermocouple protection	Mullite	Lenton	4	6	46

Table D-1. Dimensions of furnace assembly components

APPENDIX -E

CHEMICAL ANALYSIS AND SUPPLIERS OF MATERIALS

Pure gases.

Gas	Supplier	Analysis
CO	Afrox	99.97%
CO_2	Afrox	99.995%
Ar	Afrox	99.999%

Liquid charge

Liquid	Supplier	Analysis
SO_2	Chemical Initiatives	99.9%

Solid charge

Solid	Supplier	Analysis
Ni_3S_2 powder	Sigma-Aldrich	99.7%
Cu_2S powder	Sigma-Aldrich	
FeS grained	Saarchem	
SiO_2 powder	Saarchem	

Cr powder Si C Fe Al S O N	Industrial Analytical	99% 0.014% 0.016% 0.11% 0.0062% 0.028% 0.74% 0.036%
Cr_2O_3 powder	Merck	99%
Ag crystals	Aldrich Chemicals Co.	99.99 +%
Fe electrolytic	BDH Chemicals Ltd.	
Iron (III) oxide [Fe_2O_3]: CO Na Cu Ca Mn Mg		99.98% 13.2 ppm 12.1 ppm 9.7 ppm 3.6 ppm 2.3 ppm 1.2 ppm
Iron (II) oxalate dihydrate [$C_2FeO_4.2H_2O$]: Heavy metals (as Pb) Chloride (Cl) Sulfate (SO_4)	Sigma-Aldrich	99% Max 0.01% Max 0.005% Max 0.1%

Fe wire C Mn P S Si Cr V Cu Ni	Industrial Analytical	99+% 0.06% 0.39% 0.007% 0.003% 0.1% 0.0% 0.0% 0.0% 0.0%
Pt wire	Temperature Control	99.999%

APPENDIX –F

PREPARATION OF LABORATORY IRON OXIDE

Among all the components used in the experiment, FeO was obtained from an Iron (II) oxalate dihydrate [$C_2FeO_4.2H_2O$]. The principle consisted of obtaining FeO from $FeC_2O_4.2H_2O$ by using a muffle furnace at 1000^{o}C according to the reaction:

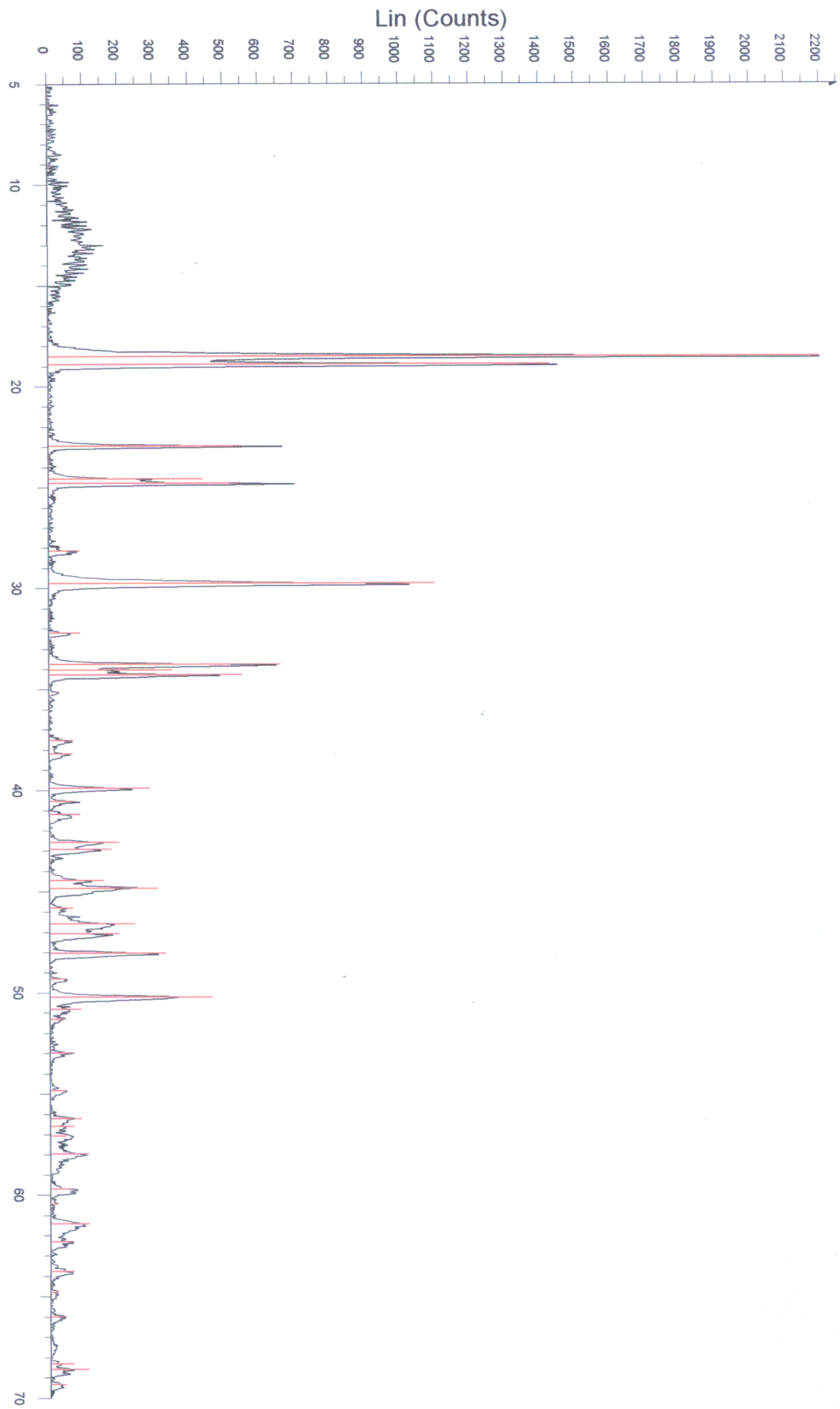
$$FeC_2O_4.2H_2O_{[S]} \xrightarrow{Ar} FeO_{[S]} + CO_{[g]} + CO_{2\,[g]} + 2H_2O_{[g]}$$

Each test was run at constant argon potential of 1atm.

The charge usually weighed around 10mg depending on the capacity of the iron crucible and was made from commercially produced $FeC_2O_4.2H_2O$.

The furnace was preflushed with argon gas for 20 minutes to ensure that all the air and impurities had been expelled. The iron crucible was placed in the furnace along with the iron (II) oxalate dihydrate for 20 minutes and quenched in the argon atmosphere for 20 minutes. The FeO obtained weighed approximately 4mg.

XRD tests of $FeC_2O_4.2H_2O$, Fe_sSiO_4, FeO are shown in the figures F-1, F-2 and F-3.



t

Figure F-1. XRD of $FeC_2O_4.2H_2O$

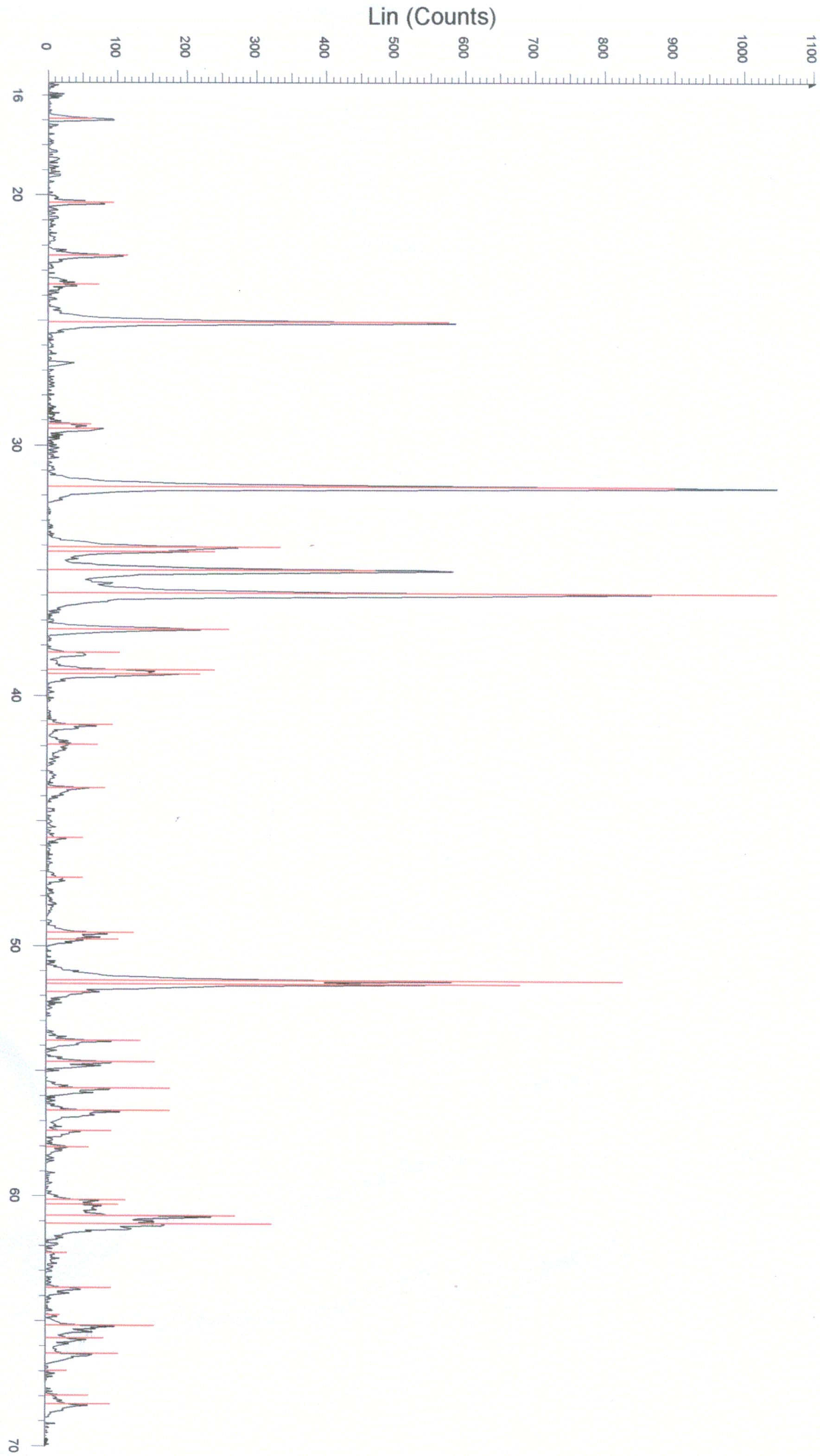


Figure F-2. XRD of Fe_2SiO_4

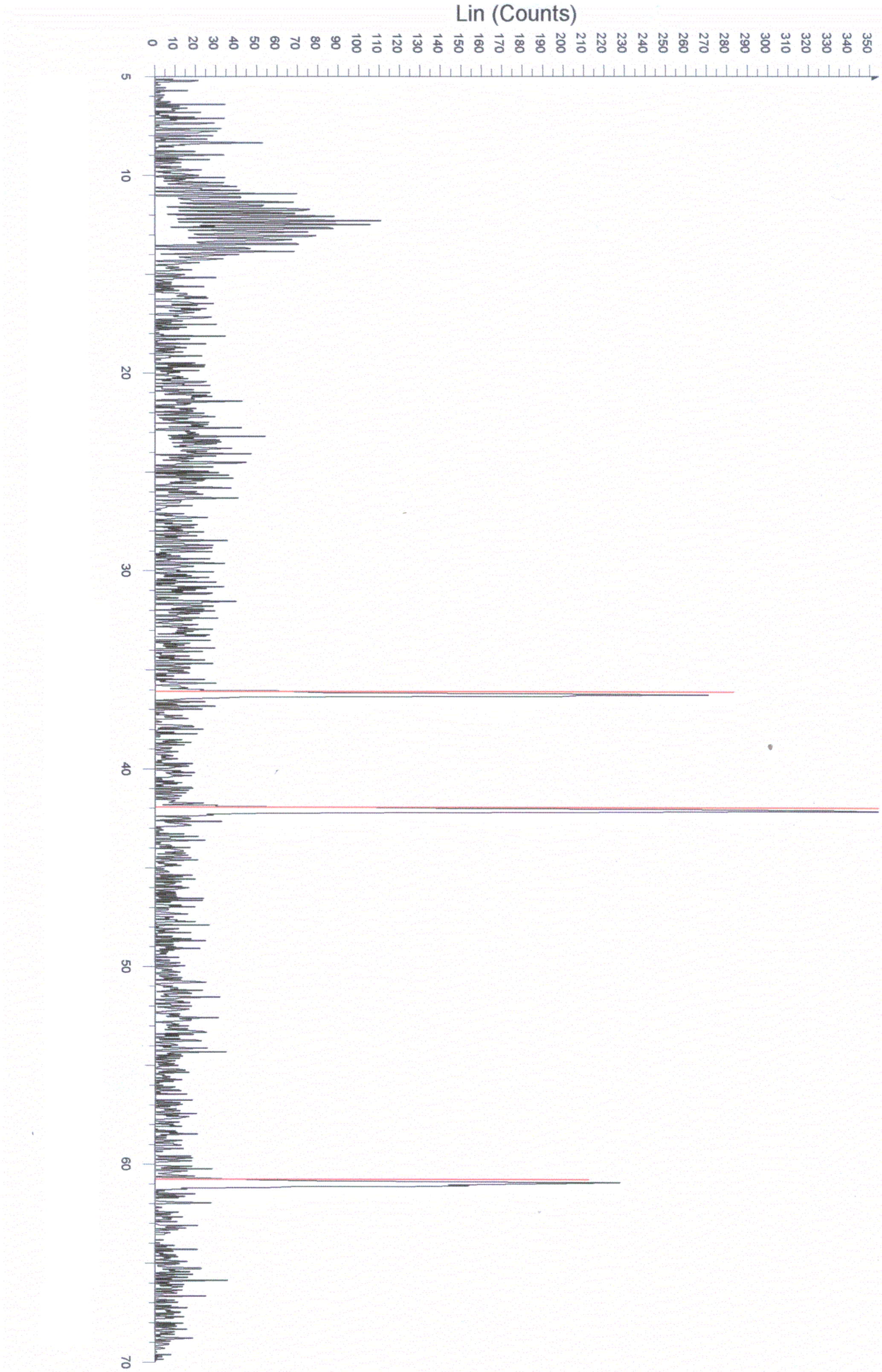


Figure F-3. XRD of FeO

APPENDIX -G

SPECIFICITY OF DIGITAL READOUT AND CONTROL SYSTEM E-7000.

-Gas flow

The Bronkhorst High-Tech B.V. series mass flow meter for gases is an accurate device for measuring gas flows up to 700 bar depending on body rating, virtually independent of pressure and temperature changes. The digital readout can measure and control gas flows from 3 ml_N/h up to several thousand m^3_N /h.

-Liquid flow

The Bronkhorst High-Tech B.V. series mass flow meter for liquids is an accurate device for measuring gas flows up to 400 bars, virtually independent of pressure and temperature changes. The system can be completed with a control valve to measure and control liquid flows from less than a gram per hour up to 20 kg/h.

-Pressure

The Bronkhorst High-Tech B.V. pressure meter measures pressures from 100 mbar up to 400 bar depending on body rating, either absolute pressure or gauge pressure and in the range 0 to 15-bar differential pressure too. The flow going through the pressure controller depends on up and downstream pressures, the orifice diameter of the valve and kind of fluid.

The gas mixing system shown below represents a

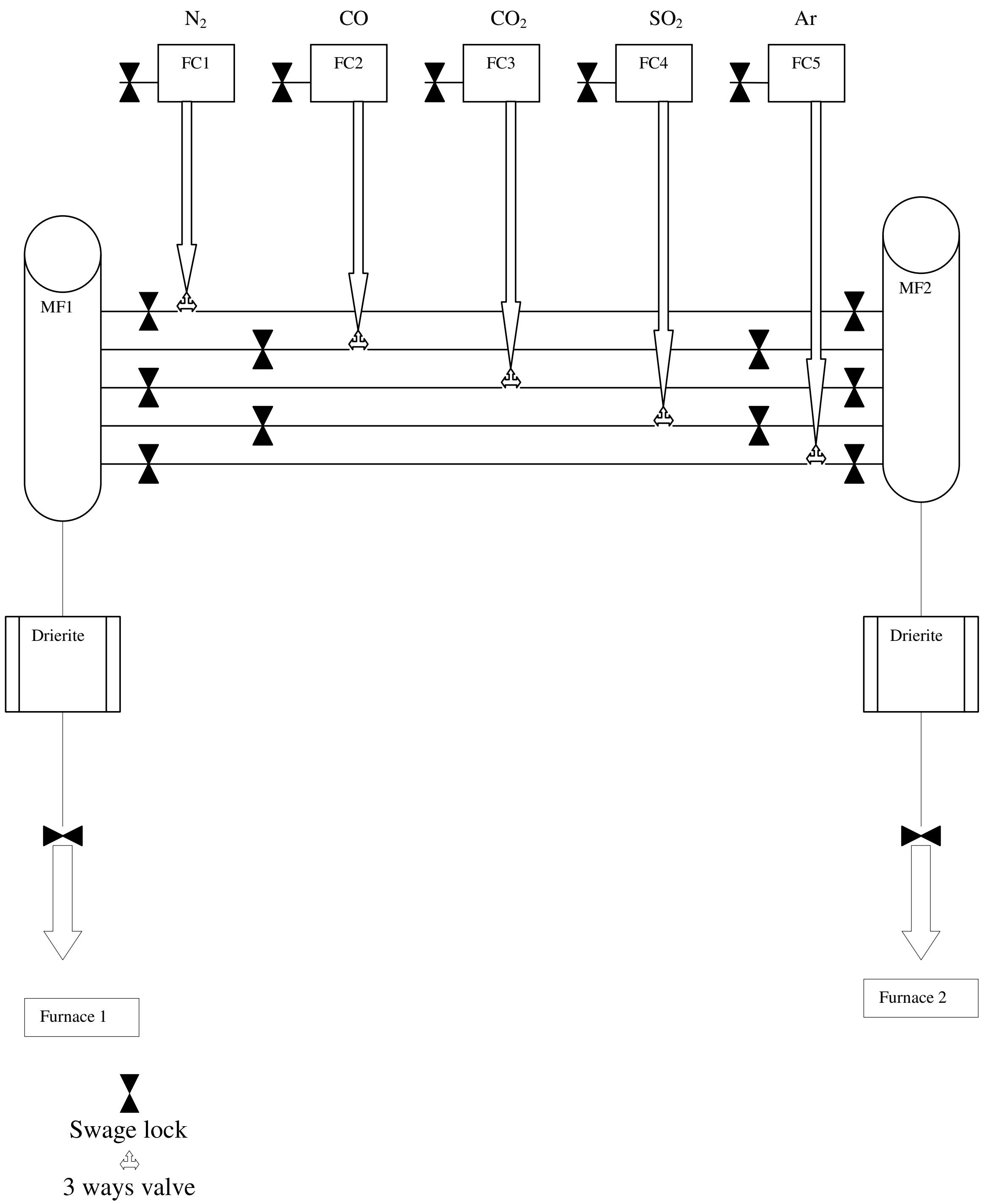


Figure G-1. Schematic representation of the gas mixing system

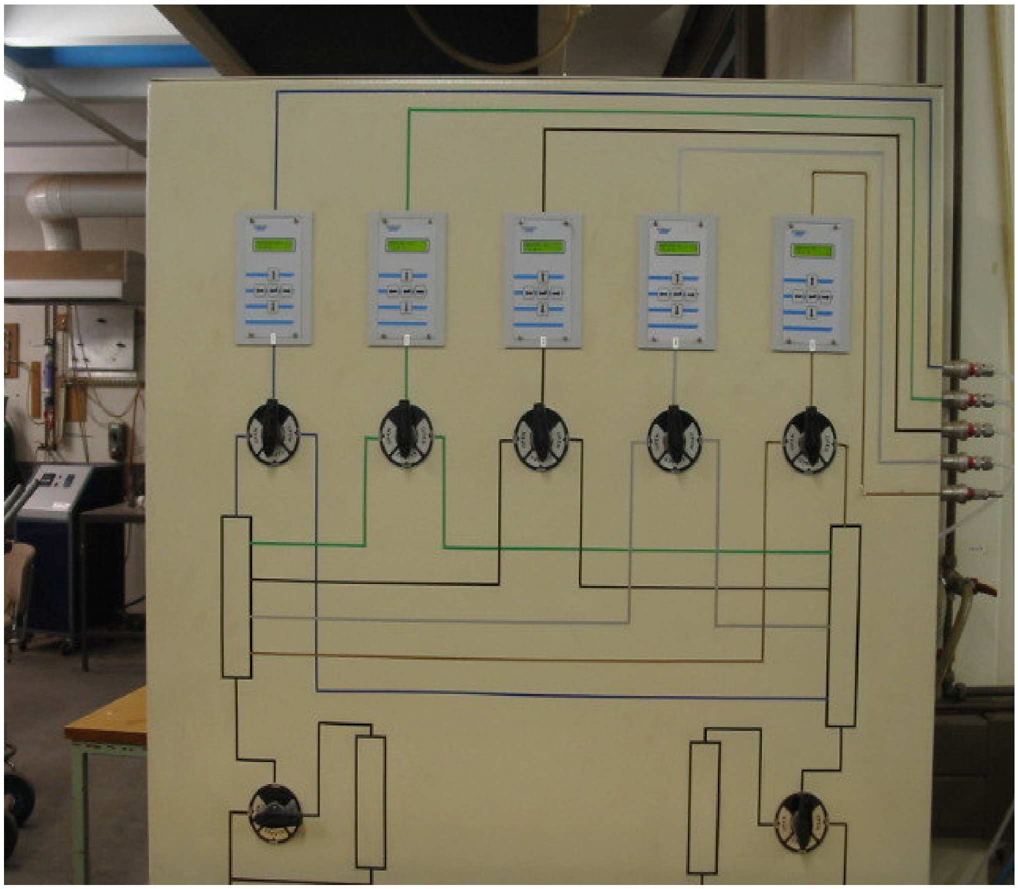


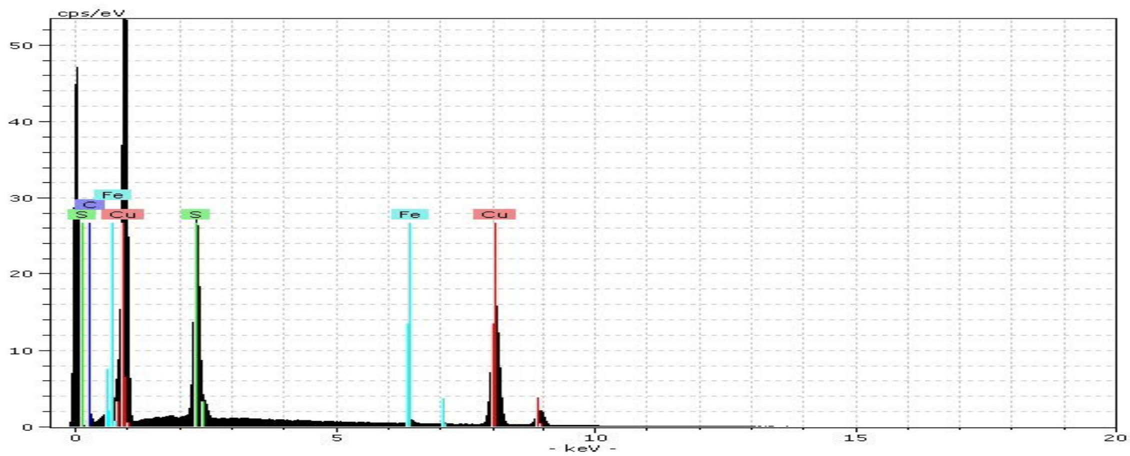
Figure G-2. Picture of gas mixing system used in these experiments.

APPENDIX-H

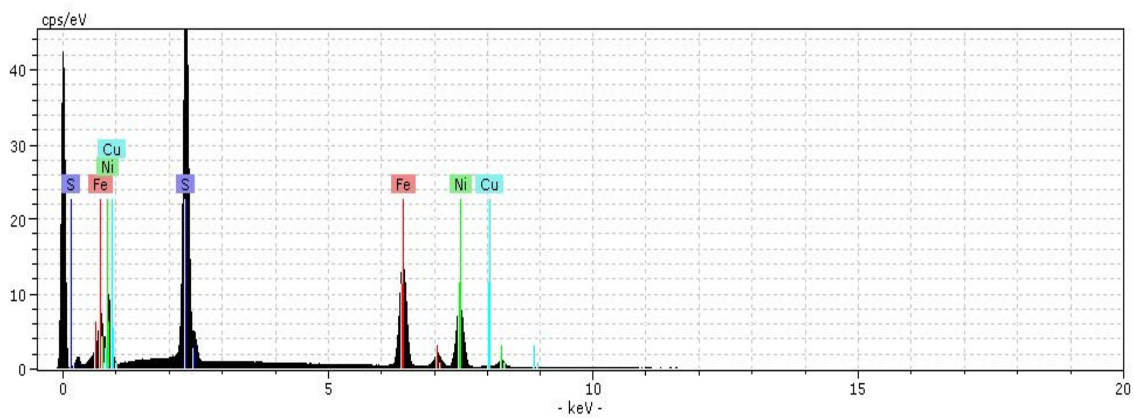
SPECTRO AND TABLES WITH ELECTRON PROBE MICROANALYSER.

This chapter presents the analyses presented as spectra obtained with the electron probe microanalyser CAMECA SX 100.

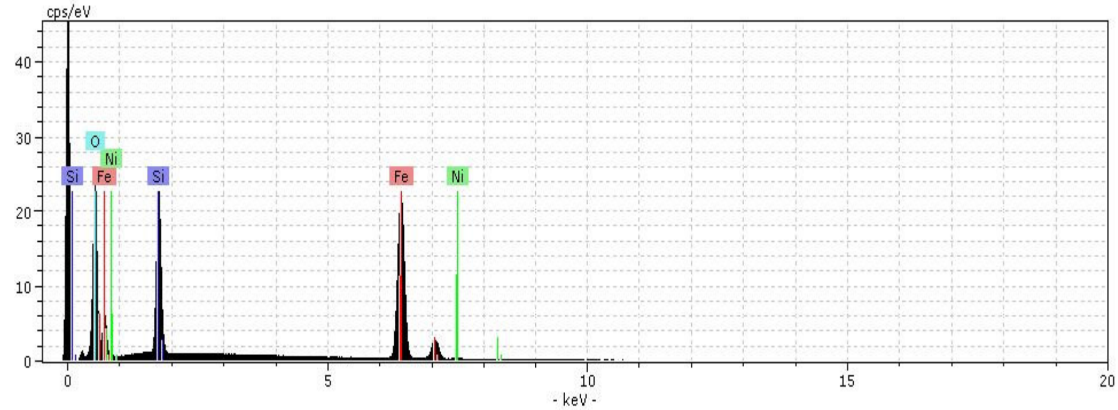
H.1. Spectra



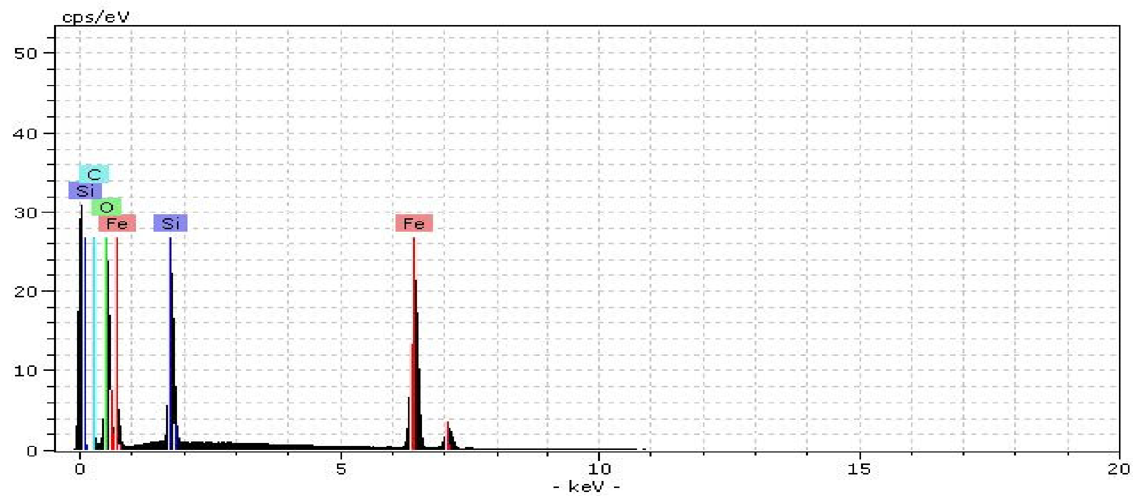
Cu-sulphide-Cr_2O_3-test2



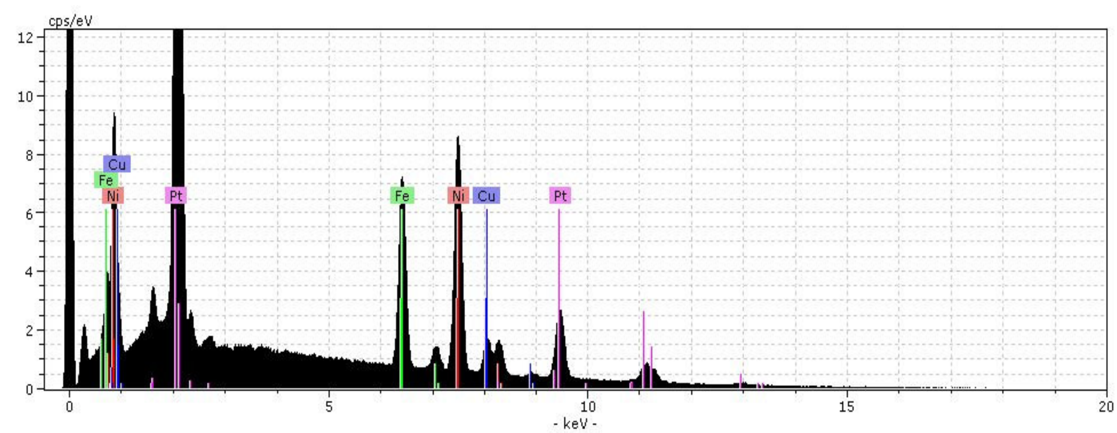
NiFe-sulphide-Fe_2O_3-test14



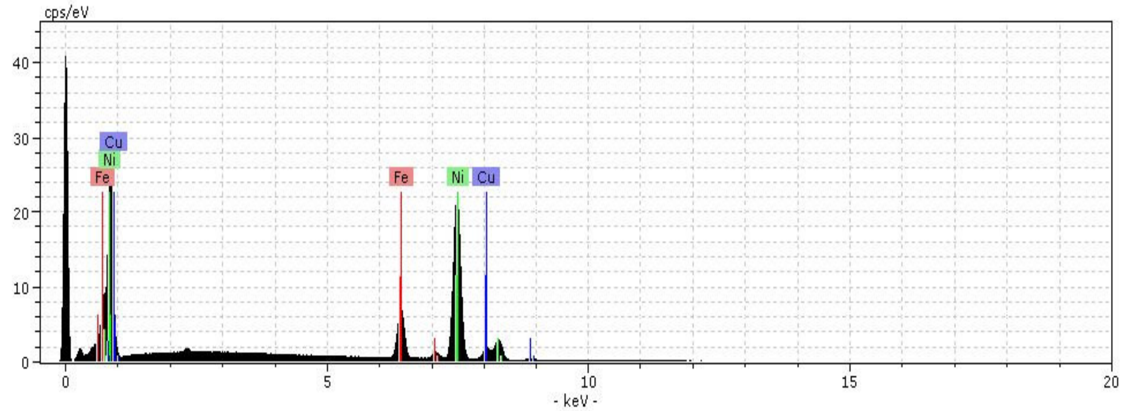
Fe_silicate-Fe_2O_3-test14



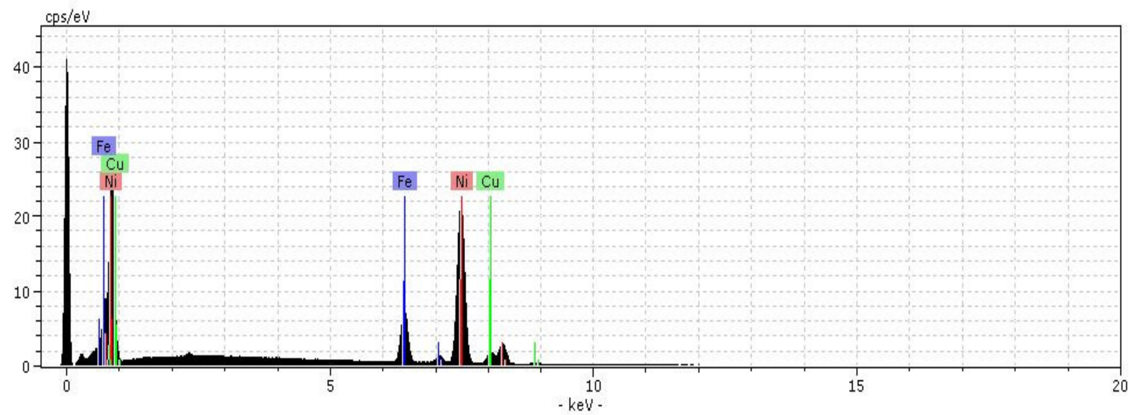
Fe_silicate-Fe_2O_3-test5



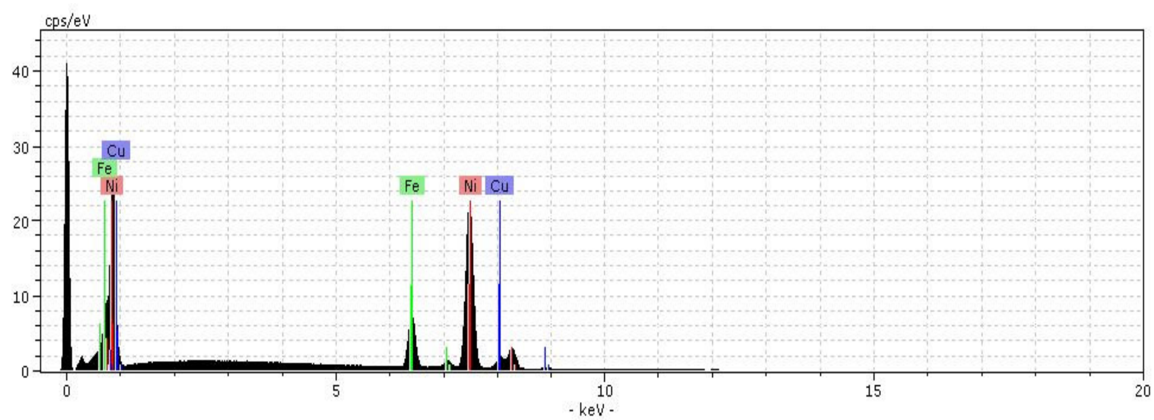
Alloy 1+Pt-Cr_2O_3-test2



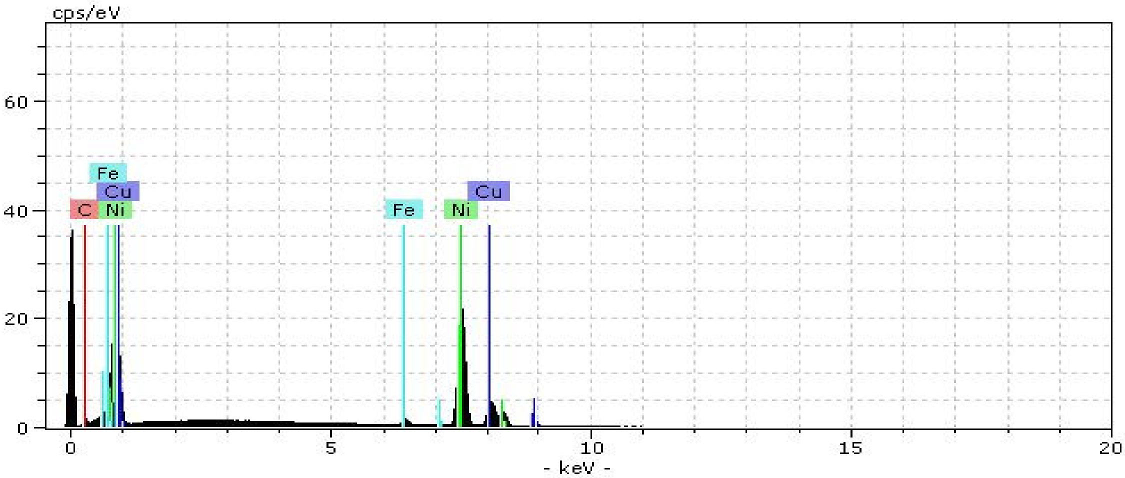
Alloy FeNiCu-Fe_2O_3-test14



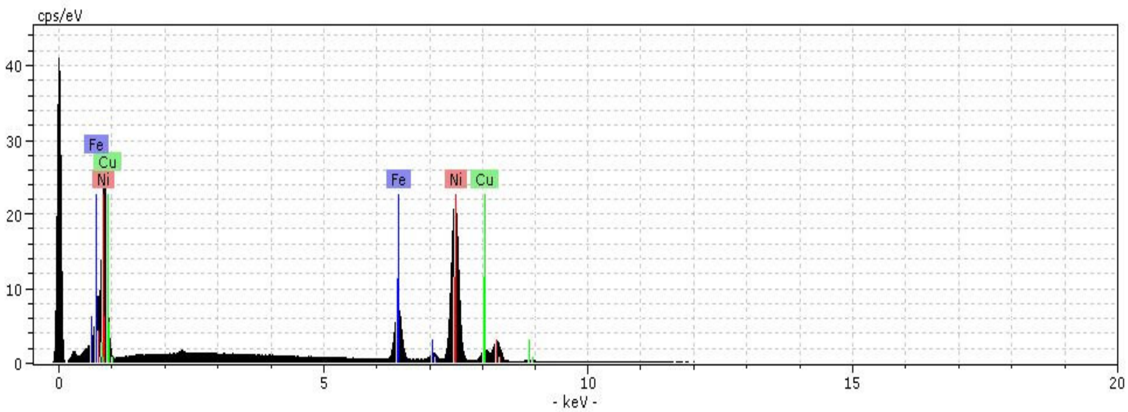
NiFeCu-alloy-Fe_2O_3-test12



NiFeCu-alloy-Fe_2O_3-test13



NiCuFe_alloy-Fe_2O_3-test10



NiCuFe_alloy-Fe_2O_3-test12

Tables.

SiO_2-Cr_2O_3-test1

Element	Silicon	Oxygen	Iron	
Series	K series	K series	K series	
Net	301993	71781	1487	
unnor. wt. %	48.09	63.23	0.76	
norm. wt. %	42.90	56.42	0.68	100.00
at. %	30.15	69.61	0.24	100.00

Fe-Silicate-Cr_2O_3-test3

Element	Silicon	Oxygen	Iron	
Series	K series	K series	K series	
Net	67583	66020	114189	
unnor. wt. %	12.64	33.18	54.51	
norm. wt. %	12.59	33.07	54.33	100.00
at. %	12.85	59.26	27.89	100.00

Fe_2SiO_4-FeO-test5					
Element	***Carbon***	***Iron***	***Oxygen***	***Silicon***	
Series	K series	K series	K series	K series	
Net	9635	224216	127118	131900	
unnor. wt. %	3.407111	52.81801	33.10996	12.29493	
norm. wt. %	3.352465	51.97088	32.57892	12.09774	100
at. %	7.591456	25.31047	55.38255	11.71553	100

Fe_2SiO_4-FeO-test7b

Element	***Carbon***	***Iron***	***Oxygen***	***Silicon***	***Nickel***	
Series	K series	K series	K series	K series	K series	
Net	8868	222337	131316	134382	8458	
unnor. wt. %	3.039019	51.27874	32.85132	12.19988	3.081481	
norm. wt. %	2.96633	50.05224	32.06557	11.90808	3.007777	100
at. %	6.817382	24.74007	55.32387	11.70407	1.4146	100

Fe_2SiO_4-Fe_2O_3-test12

Element	***Iron***	***Oxygen***	***Silicon***	***Nickel***	
Series	K series	K series	K series	K series	
Net	225557	133853	132135	3843	
unnor. wt. %	54.30947	33.26472	12.38302	1.479027	
norm. wt. %	53.5405	32.79373	12.20769	1.458086	100
at. %	27.64505	59.10469	12.5339	0.716356	100

Fe_2SiO_4-Fe_2O_3-test13b

Element	***Iron***	***Oxygen***	***Silicon***	***Nickel***	
Series	K series	K series	K series	K series	
Net	227866	133106	133063	3197	
unnor. wt. %	55.62319	32.94222	12.66261	1.231222	
norm. wt. %	54.28811	32.15154	12.35868	1.20167	100
at. %	28.24072	58.38065	12.78383	0.594794	100

Cu-sulphide-Cr_2O_3-test2

Element	***Sulfur***	***Copper***	***Iron***	
Series	K series	K series	K series	
Net	125043	78916	20352	
unnor. wt. %	21.54133	63.92146	7.08732	
norm. wt. %	23.27531	69.06687	7.6578195	100
at. %	37.22613	55.74149	7.0323802	100

Cu-sulphide-Cr_2O_3-test1

Element	***Sulfur***	***Copper***	***Iron***	
Series	K series	K series	K series	
Net	101539	93927	3028	
unnor. wt. %	18.17155	75.25997	0.9443648	
norm. wt. %	19.25444	79.74492	1.0006421	100
at. %	32.0538	66.98973	0.9564721	100

Ni-sulphide-Cr_2O_3-test3

Element	***Nickel***	***Sulfur***	***Iron***	
Series	K series	K series	K series	
Net	41083	52588	738	
unnor. wt. %	75.66	24.26	0.60	
norm. wt. %	75.26	24.14	0.60	100.00
at. %	62.68	36.79	0.52	100.00

FeNi-sulphide-Cr_2O_3-test3

Element	*Carbon*	*Nickel*	*Sulfur*	*Copper*	*Iron*	
Series	K series	K series	K series	K series	K series	
Net	6797	46695	183326	1219	71342	
unnor. wt. %	6.15	31.78	29.49	0.99	29.30	
norm. wt. %	6.30	32.53	30.18	1.02	29.98	100.00
at. %	20.38	21.54	36.58	0.62	20.87	100.00

Cu-sulphide-FeO-test8

Element	*Carbon*	*Nickel*	*Sulfur*	*Copper*	*Iron*	
Series	K series	K series	K series	K series	K series	
Net	14364	4506	200214	187665	4677	
unnor. wt. %	7.245635	1.211249	16.91023	69.77298	0.6814194	
norm. wt. %	7.561594	1.264068	17.64764	72.81557	0.711134	100
at. %	26.67551	0.912557	23.31956	48.55283	0.539548	100

Cu-sulphide-FeO-test5

Element	*Carbon*	*Sulfur*	*Copper*	*Iron*	*Oxygen*	
Series	K series	K series	K series	K series	K series	
Net	12832	200942	182457	7655	13735	
unnor. wt. %	6.061333	16.87425	70.64997	1.1563649	5.2766149	
norm. wt. %	6.06021	16.87112	70.63688	1.1561506	5.2756371	100
at. %	20.24114	21.10695	44.5933	0.8305024	13.228103	100

FeNi sulphide-FeO-test6c

Element	*Carbon*	*Nickel*	*Sulfur*	*Copper*	*Iron*	
Series	K series	K series	K series	K series	K series	
Net	14160	61534	335878	38965	137635	
unnor. wt. %	6.025214	20.39458	27.2543	15.62146	27.760996	
norm. wt. %	6.207941	21.01309	28.08085	16.09522	28.602905	100
at. %	20.54239	14.22929	34.80551	10.06679	20.35602	100

Cu-sulphide-FeO-test8

Element	*Carbon*	*Nickel*	*Sulfur*	*Copper*	*Iron*	
Series	K series	K series	K series	K series	K series	
Net	15200	214006	271599	3882	9637	
unnor. wt. %	6.441028	69.94797	22.80767	1.53399	1.4349162	
norm. wt. %	6.304499	68.46531	22.32422	1.501475	1.4045007	100
at. %	21.5442	47.87847	28.57528	0.969815	1.0322409	100

Cu-sulphide-FeO-test5

Element	*Carbon*	*Sulfur*	*Copper*	*Iron*	*Oxygen*	
Series	K series	K series	K series	K series	K series	
Net	12122	237040	162243	31105	12973	
unnor. wt. %	5.914864	19.52303	62.2656	5.0478409	5.1325189	
norm. wt. %	6.042737	19.9451	63.61171	5.1569699	5.2434785	100
at. %	19.75881	24.42856	39.31473	3.6266121	12.871292	100

Cu-sulphide-FeO-test10

Element	*Carbon*	*Nickel*	*Sulfur*	*Copper*	*Iron*	
Series	K series	K series	K series	K series	K series	
Net	11818	2696	201236	190218	3107	
unnor. wt. %	6.021697	0.734389	17.27395	72.26865	0.4584873	
norm. wt. %	6.223514	0.759002	17.85289	74.69074	0.4738536	100
at. %	22.80893	0.569248	24.50824	51.74007	0.3735018	100

Ni sulphide-Fe_2O_3-test12

Element	*Nickel*	*Sulfur*	*Iron*	
Series	K series	K series	K series	
Net	216170	272644	1236	
unnor. wt. %	73.03065	23.94372	0.1857524	
norm. wt. %	75.16525	24.64356	0.1911817	100
at. %	62.39147	37.44175	0.1667799	100

Ni sulphide-Fe_2O_3-test10

Element	*Carbon*	*Nickel*	*Sulfur*	
Series	K series	K series	K series	
Net	12497	218211	279479	
unnor. wt. %	5.630103	69.89387	23.1157	
norm. wt. %	5.707747	70.85777	23.43448	100
at. %	19.69143	50.02533	30.28324	100

FeNi sulphide-Fe_2O_3-test12

Element	***Nickel***	***Sulfur***	***Copper***	***Iron***	
Series	K series	K series	K series	K series	
Net	92839	360065	3284	140425	
unnor. wt. %	33.63138	30.45018	1.428904	30.400615	
norm. wt. %	35.06517	31.74834	1.489822	31.696668	100
at. %	27.42351	45.44777	1.076174	26.052544	100

Cu-sulphide-Fe_2O_3-test12

Element	***Nickel***	***Sulfur***	***Copper***	***Iron***	
Series	K series	K series	K series	K series	
Net	1945	200364	186309	5561	
unnor. wt. %	0.55292	17.98237	73.75973	0.8592595	
norm. wt. %	0.593553	19.30385	79.18019	0.9224048	100
at. %	0.539445	32.11265	66.46686	0.881046	

Cu-sulphide-Fe_2O_3-test10

Element	***Carbon***	***Sulfur***	***Copper***	
Series	K series	K series	K series	
Net	10760	203512	191180	
unnor. wt. %	5.692978	17.01654	72.3323	
norm. wt. %	5.989972	17.90427	76.10576	100
at. %	22.11844	24.76399	53.11757	100

Ni sulphide-FeO-test9

Element	***Carbon***	***Nickel***	***Sulfur***	***Copper***	***Iron***	
Series	K series	K series	K series	K series	K series	
Net	13909	214008	268736	5274	2311	
unnor. wt. %	6.102027	69.74933	22.17335	2.085459	0.3331947	
norm. wt. %	6.075093	69.44145	22.07548	2.076254	0.331724	100
at. %	20.93546	48.97093	28.49536	1.352387	0.2458588	100

Ni sulphide-FeO-test5

Element	***Carbon***	***Nickel***	***Sulfur***	
Series	K series	K series	K series	
Net	14567	213793	271927	
unnor. wt. %	6.52962	70.83415	22.88699	
norm. wt. %	6.513287	70.65697	22.82974	100
at. %	22.06109	48.97468	28.96423	100

Ni sulphide-FeO-test8

Element	*Carbon*	*Nickel*	*Copper*	*Iron*	
Series	K series	K series	K series	K series	
Net	19574	236991	58113	11471	
unnor. wt. %	7.123416	70.97782	21.27806	1.3831352	
norm. wt. %	7.069516	70.44076	21.11705	1.3726696	100
at. %	27.43195	55.93465	15.48786	1.1455454	100

FeNi sulphide-FeO-test6a

Element	*Carbon*	*Nickel*	*Sulfur*	*Copper*	*Iron*	
Series	K series	K series	K series	K series	K series	
Net	12892	28527	415105	5444	217788	
unnor. wt. %	5.711504	10.08586	32.84074	2.296138	48.637991	
norm. wt. %	5.736041	10.12919	32.98182	2.306002	48.846946	100
at. %	18.44132	6.664143	39.71814	1.401298	33.775095	100

Ni sulphide-Fe_2O_3-test11

Element	*Carbon*	*Nickel*	*Sulfur*	*Iron*	
Series	K series	K series	K series	K series	
Net	12220	217473	275852	1295	
unnor. wt. %	5.610731	68.12894	22.69177	0.181969	
norm. wt. %	5.807405	70.51707	23.48718	0.1883476	100
at. %	19.9731	49.63038	30.2572	0.1393166	100

NiFe sulphide-Fe_2O_3-test14

Element	*Nickel*	*Sulfur*	*Copper*	*Iron*	
Series	K series	K series	K series	K series	
Net	92261	358891	2544	144277	
unnor. wt. %	33.30998	30.44098	1.101625	31.26799	
norm. wt. %	34.65437	31.66958	1.146086	32.529965	100
at. %	27.10153	45.33385	0.827855	26.736764	100

NiCu sulphide-Fe_2O_3-test10

Element	*Carbon*	*Nickel*	*Sulfur*	*Copper*	*Iron*
Series	K series	K series	K series	K series	K series
Net	14791	5475	197619	190095	1391
unnor. wt. %	7.430626	1.459024	16.19815	70.5752	0.197098
norm. wt. %	7.751532	1.522035	16.8977	73.62312	0.20561
at. %	27.34003	1.098566	22.32407	49.08136	0.1559678

Ni sulphide-Fe_2O_3-test14

Element	Nickel	Sulfur	Iron	
Series	K series	K series	K series	
Net	215553	272712	1399	
unnor. wt. %	73.48194	23.65563	0.2108884	
norm. wt. %	75.48342	24.29995	0.2166325	100
at. %	62.80364	37.00693	0.1894289	100

SiO_2-Fe_2O_3-test14a

Element		Iron	Oxygen	Silicon	Nickel	
Series		K series	K series	K series	K series	
Net		3443	138755	597397	898	
unnor. wt. %		0.938052	62.85777	49.82189	0.352879	
norm. wt. %		0.823065	55.15263	43.71469	0.309623	100
at. %		0.293368	68.61856	30.98306	0.105008	100

SiO_2-Fe_2O_3-test13a

Element		Iron	Oxygen	Silicon	
Series		K series	K series	K series	
Net		3108	143200	599482	
unnor. wt. %		0.827867	64.90356	53.3052	
norm. wt. %		0.695473	54.52403	44.7805	100
at. %		0.24833	67.95688	31.79479	100

$FeNiSiO_2$-Fe_2O_3-test10

Element	Carbon	Iron	Oxygen	Silicon	Nickel	
Series	K series	K series	K series	K series	K series	
Net	7778	192567	129519	132269	29438	
unnor. wt. %	2.689208	43.59758	32.46247	12.26465	10.53772	
norm. wt. %	2.648119	42.93145	31.96647	12.07725	10.37671	100
at. %	6.134516	21.38935	55.59208	11.96487	4.919179	100

Fe_2SiO_4-Fe_2O_3-test14b

Element	Iron	Oxygen	Silicon	Nickel	
Series	K series	K series	K series	K series	
Net	224430	131861	132996	3369	
unnor. wt. %	52.78615	33.1882	12.30762	1.250117	
norm. wt. %	53.03431	33.34422	12.36548	1.255994	100
at. %	27.1681	59.62373	12.59595	0.61221	100

SiO_2-FeO-test5a

Element	Carbon	Iron	Oxygen	Silicon	Aluminium	Potassium	Sodium	Titanium
Series	K series	K series	K series	K series	K series	K series	K series	K series
Net	396	30553	102787	374329	52291	24193	4164	3447
unnor. wt. %	0.289263	8.325343	53.89242	37.05329	5.3835465	2.9759491	0.792364	0.502114
norm. wt. %	0.258596	7.442691	48.17875	33.1249	4.8127837	2.6604394	0.708358	0.44888
at. %	0.46221	2.861059	64.64703	25.32032	3.8293613	1.4608049	0.661477	0.201267

SiO_2-FeO-test7

Element	Carbon	Iron	Oxygen	Silicon
Series	K series	K series	K series	K series
Net	4153	3847	155524	605161
unnor. wt. %	2.43688	0.972912	63.82991	42.96969
norm. wt. %	2.211136	0.882785	57.91694	38.98914
at. %	3.534753	0.303513	69.50639	26.65534

SiO_2-FeO-test5b

Element	Carbon	Iron	Oxygen	Silicon
Series		K series	K series	K series
Net	2770	144596	596083	
unnor. wt. %	0.70676	62.4732	43.86304	
norm. wt. %	0.660258	58.36272	40.97703	100
at. %	0.230972	71.26516	28.50387	100

Fe_2SiO_4-FeO-test7a

Element	***Carbon***	***Iron***	***Oxygen***	***Silicon***	***Nickel***	
Series	K series	K series	K series	K series	K series	
Net	8404	233795	131924	133967	1043	
unnor. wt. %	2.88576	55.55626	32.90566	12.08489	0.396013	
norm. wt. %	2.77935	53.50768	31.69229	11.63927	0.38141	100
at. %	6.443404	26.67887	55.15707	11.53971	0.180948	100

Pt-alloy-FeO-test5

Element	***Carbon***	***Iron***	***Copper***	***Nickel***	***Platinum***	
Series	K series	K series	K series	K series	M series	
Net	20776	45958	24539	104517	269367	
unnor. wt. %	14.79939	8.882061	8.227377	29.3223	38.93146	
norm. wt. %	14.77537	8.867643	8.214022	29.27471	38.86826	100
at. %	55.50694	7.164676	5.832514	22.50564	8.990225	100

Pt-alloy2-FeO-test5

Element	***Carbon***	***Iron***	***Copper***	***Nickel***	***Platinum***	
Series	K series	K series	K series	K series	M series	
Net	20329	53670	18604	141231	197306	
unnor. wt. %	7.972933	10.92009	6.747346	42.7086	31.234	
norm. wt. %	8.006321	10.96582	6.775603	42.88746	31.3648	100
at. %	35.81765	10.55078	5.729318	39.26307	8.639188	100

Ni-alloy-FeO-test5

Element	***Carbon***	***Iron***	***Copper***	***Nickel***	
Series	K series	K series	K series	K series	
Net	19117	62329	19771	243292	
unnor. wt. %	7.101207	8.989218	7.596674	77.14862	
norm. wt. %	7.042353	8.914716	7.533714	76.50922	100
at. %	27.04392	7.362727	5.468295	60.12506	100

FeNiCu-alloy-FeO-test9

Element	Iron	Copper	Nickel	
Series	K series	K series	K series	
Net	30968	40217	248351	
unnor. wt. %	4.244951	15.95614	80.69308	
norm. wt. %	4.20733	15.81473	79.97794	100
at. %	4.466128	14.7536	80.78027	100

NiCuFe-alloy-Fe_2O_3-test14

Element	Iron	Copper	Nickel	
Series	K series	K series	K series	
Net	71244	20248	243143	
unnor. wt. %	11.33568	8.146723	81.72458	
norm. wt. %	11.20049	8.049566	80.74994	100
at. %	11.77651	7.438133	80.78535	100

NiCuFe-alloy-Fe_2O_3-test13

Element	Iron	Copper	Nickel	
Series	K series	K series	K series	
Net	75739	19555	244179	
unnor. wt. %	11.92795	7.96426	82.12681	
norm. wt. %	11.69189	7.806642	80.50147	100
at. %	12.28783	7.210516	80.50165	100

NiCuFe-alloy-Fe_2O_3-test12

Element	Iron	Copper	Nickel	
Series	K series	K series	K series	
Net	75948	18702	241238	
unnor. wt. %	12.27783	7.637082	82.31995	
norm. wt. %	12.00944	7.470134	80.52043	100
at. %	12.61628	6.896815	80.4869	100

NiCu-alloy-Fe_2O_3-test10a

Element	Carbon	Copper	Nickel	
Series	K series	K series	K series	
Net	16119	146193	132696	
unnor. wt. %	6.671596	51.90846	37.53212	
norm. wt. %	6.941468	54.0082	39.05033	100
at. %	27.61021	40.60401	31.78578	100

NiCu-alloy-Fe_2O_3-test10b

Element	***Carbon***	***Copper***	***Nickel***	
Series	K series	K series	K series	
Net	14526	213590	49651	
unnor. wt. %	6.19427	73.03698	12.93144	
norm. wt. %	6.721017	79.24789	14.0311	100
at. %	27.35324	60.96105	11.68571	100

NiCuFe-alloy-Fe_2O_3-test13

Element	***Iron***	***Copper***	***Nickel***	***Platinum***	***Tin***	
Series	K series	K series	K series	M series	L series	
Net	55771	27075	223594	16638	23132	
unnor. wt. %	9.835246	10.30965	70.92565	2.756923	3.449148	
norm. wt. %	10.1106	10.59828	72.9113	2.834107	3.545711	100
at. %	11.07651	10.20407	76.00314	0.888852	1.827435	100

NiCuFe-alloy-Fe_2O_3-test11a

Element	***Carbon***	***Iron***	***Copper***	***Nickel***	
Series	K series	K series	K series	K series	
Net	16941	65813	21402	250088	
unnor. wt. %	5.80366	9.460456	8.197295	79.28179	
norm. wt. %	5.648704	9.207865	7.978431	77.165	100
at. %	22.66	7.944186	6.0495	63.34631	100

NiCuFe-alloy-Fe_2O_3-test11b

Element	***Carbon***	***Iron***	***Copper***	***Nickel***	
Series	K series	K series	K series	K series	
Net	16595	74534	18151	245244	
unnor. wt. %	5.783948	10.94176	6.922409	77.38512	
norm. wt. %	5.724797	10.82986	6.851615	76.59373	100
at. %	22.87802	9.308089	5.17538	62.63851	100

APPENDIX -I

XRD AND XRF OF ZIRCONIA PROBE

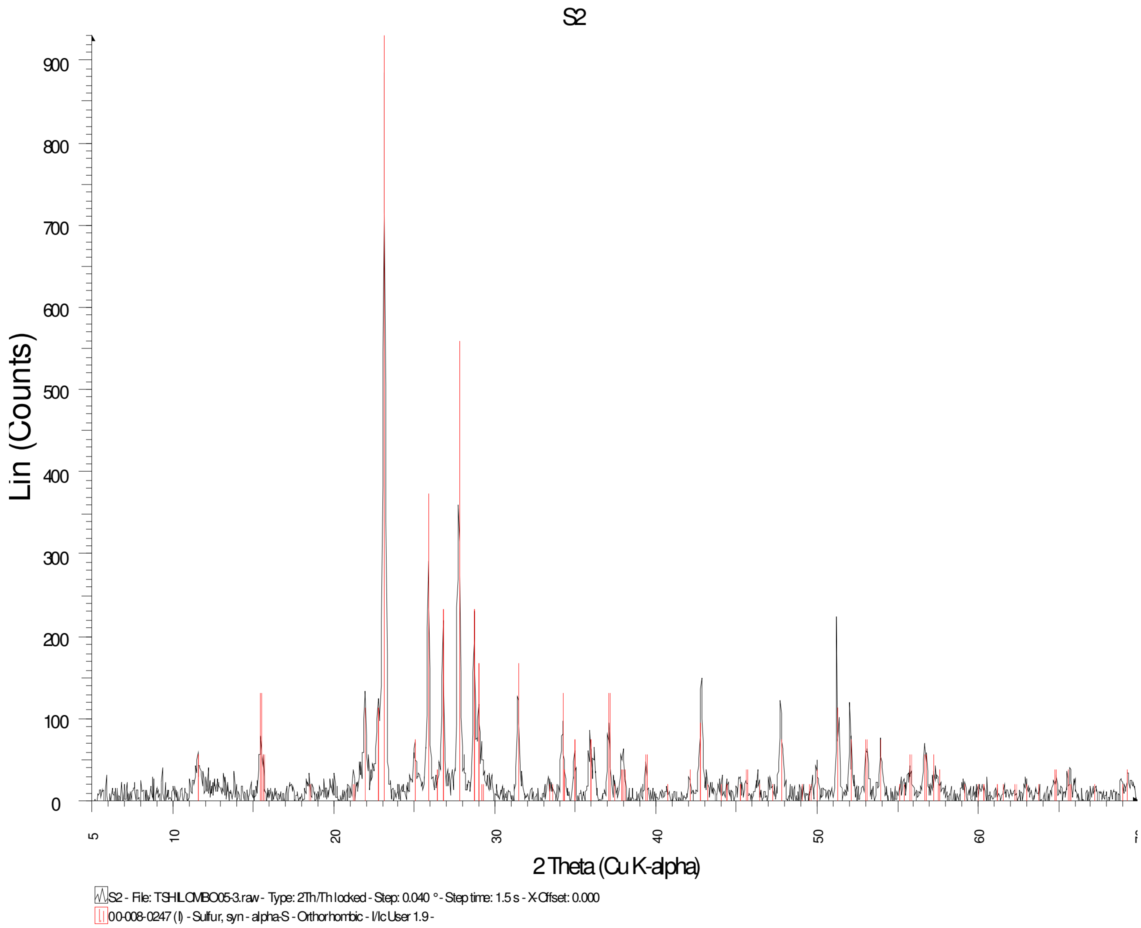


Figure I-1. XRD of sulphur content obtained in the upper level of the furnace

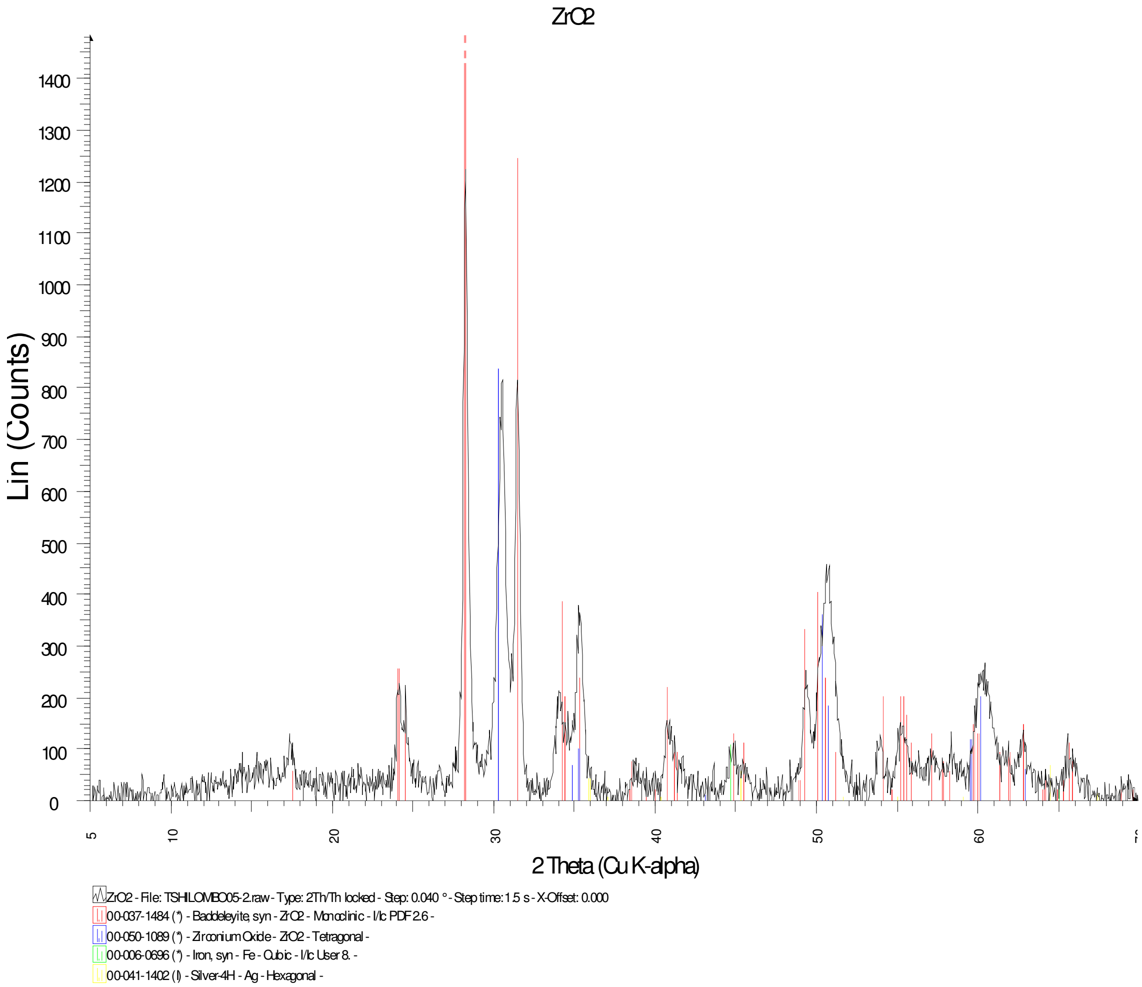


Figure I-2. XRD of zirconia probe

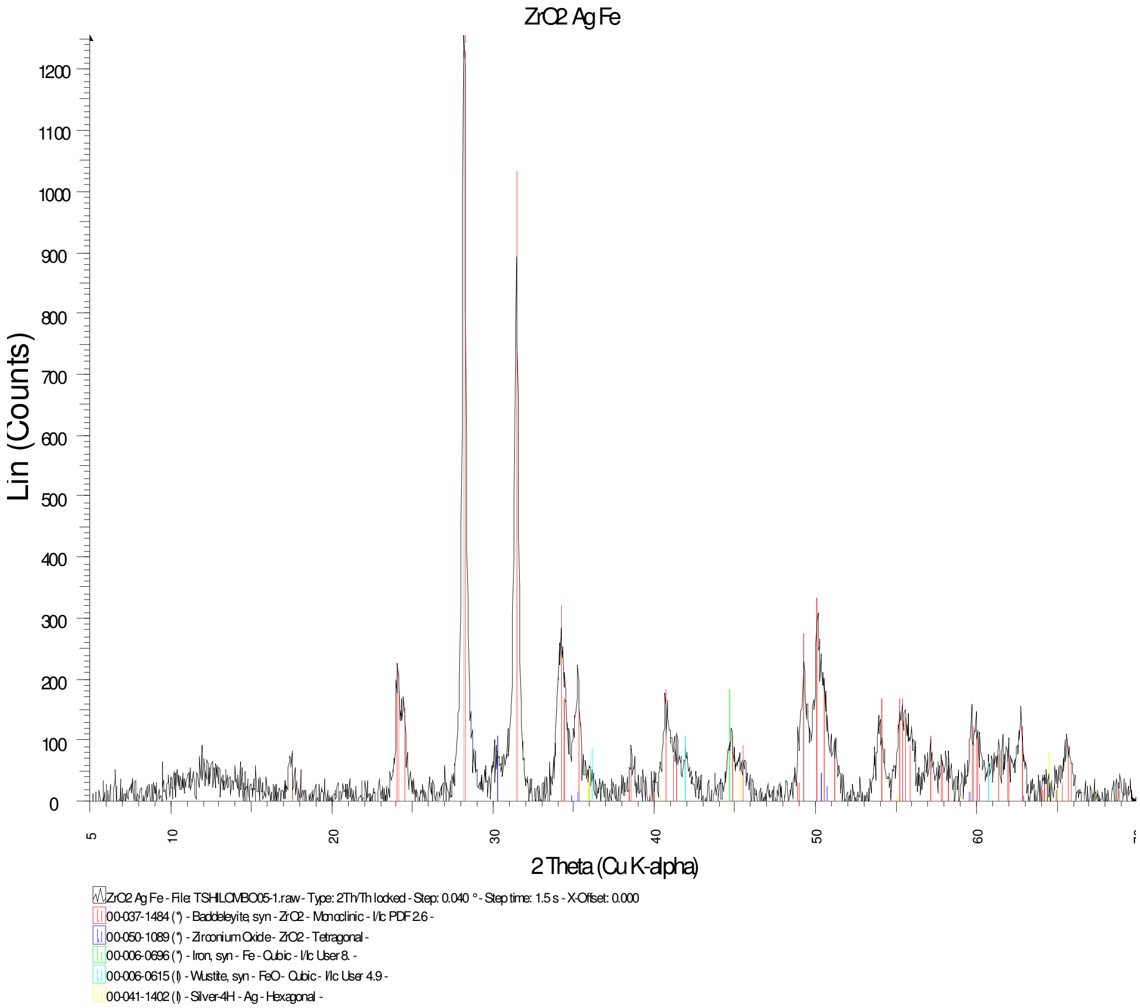


Figure I-3. XRD of zirconia probe with iron oxide, lead as part of the solid electrolyte

%	ZrO2+Ag+Fe	ZrO2
SiO_2	1.40	1.83
TiO_2	0.07	0.12
Al_2O_3	1.09	1.54
Fe_2O_3	25.74	0.50
MnO	0.031	0.015
MgO	2.975	3.372
CaO	0.30	0.31
Na_2O	1.336	1.341
K_2O		
P_2O_5		
Cr_2O_3	0.14	0.06
NiO	0.013	0.009
V_2O_5	0.02	
ZrO_2	62.94	89.22
ZnO	0.043	0.018
Nb_2O_5	0.08	0.13
CuO	0.026	0.011
Ag_2O	2.102	
HfO_2	1.153	1.296
SO_3	0.484	0.199
ThO_2	0.026	0.017
Ta_2O_5	0.020	0.027
PbO	0.019	

%	S2
S	82.90
Cu	0.907
Si	0.358
Mg	0.146
Zn	0.109
Sn	0.101
Fe	610 ppm
Pb	310 ppm
Al	200 ppm
Ni	93 ppm
Zr	72 ppm

Table I-1. XRF results of sulphur content in the upper level of the furnace, of zirconia probe and zirconia probe added with iron oxide and lead.

APPENDIX-J.

XRD RESULTS OF A MATTE SAMPLE