

TREATMENT OF A SULPHUR RICH SLUDGE AND MIXTURE WITH ZINC CONCENTRATE - USING A FLUIDISED BED REACTOR IN PILOT SCALE

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Abstract - Boliden and Swerea MEFOS have in collaboration studied and developed a process for recycling sulphur residue. Two different process concepts have been tested in the Swerea MEFOS fluidized bed pilot plant: sulphur residue was injected as a slurry and combusted, or granulated sulphur sludge was co-roasted with zinc concentrate. Optimum combustion condition for sulphur sludge and co-roasting was achieved with an oxygen coefficient of 1.2-1.3. The remaining sulphur in the calcine was analysed as metal sulphates and sulphides. There were no tendencies for sticking or sintering in the bed during the process. The process gas was found to be suitable for sulphuric acid production. The solid calcine from the sulphur sludge consists mostly of metal oxides with some sulphides or sulphates depending on the roasting conditions.

Introduction

Boliden Kokkola produces zinc via a process flow of roasting, calcine and concentrate leaching and electrowinning. From the direct zinc leaching process large quantities of a sulphur residue is generated. The sulphur residue contains about 65 wt.-% sulphur, but also valuable metals, such as zinc, lead and silver, that could be recovered. This residue is currently deposited. Direct recycling of the sulphur residue is difficult due to the nature of the material; the grain size is fine and the moisture content is high. The high sulphur content exacerbates the drying of the material since elemental sulphur is highly flammable.

A collaboration was started between Swerea MEFOS and Boliden Kokkola to find a method to treat this material such that the sulphuric content can be recycled as heat and sulphuric acid and the metal oxide content can be used for metal extraction.

It was deemed that the fluidized bed furnace pilot plant at Swerea Mefos was appropriate for these trials. The initial purpose of the pilot plant was to use it for roasting tests of primary copper concentrates with high amounts of impurities. During the course of this project the pilot plant was modified to handle higher processing temperatures making it able to perform zinc roasting.

Aim

In the roasting perspective the residual sulphur content should be at acceptable levels. It is also interesting to know how the different elements are distributed during roasting, i.e., important that the valuable metals end up in the calcine and beneficial if the impurities end up in the gas cleaning system.

Due to the flammability of the material a problem rises in safe handling from the deposit to the process. Therefore, it is crucial to find a method of preparing the material and feeding the material such that the risk of fire was non-existent or at acceptable levels.

Once confirmed that it's possible to roast the material, it's of interest to optimise the process parameters such that the best results can be achieved at the lowest cost.

The last aim is to conceive and test a possible process for co-roasting the sulphur material together with zinc concentrate. A combined process would be more flexible and the product will be easier to incorporate in the following process steps.

Material and equipment

Granulation

The granulation was done in a high intensity mixer, model Eirich RV02E. The mixer was modified such that a nitrogen atmosphere could be used to reduce the risk of ignition. The material used was dried sulphur concentrate, sulphur concentrate with 20 % moisture and zinc concentrate with 8 % moisture. Water was added to the mixer using a spray nozzle (LN ¼ SS 12 from SSC, Spraying Systems Co.). The granulated material was left out in the open to become surface dry and was later fed into the process with moisture left.

Fluidized bed reactor

An overview of the fluidized bed process can be seen in Fig. 1. The fluidized bed reactor consists of a roasting part (ID 200 mm H 2000 mm) and a freeboard (ID 300 mm H 5500 mm) made of Sandvik 253MA. Gas is introduced through a distributor plate in the bottom of the reactor and have total mixing freedom between 100 % N₂ and 100 % O₂, the gas can be pre-heated using an electric gas heater. The reactor is heated from the outside with resistor elements to mitigate heat losses due to problems of scale. Cooling of the process is possible by injecting water into the roaster part.

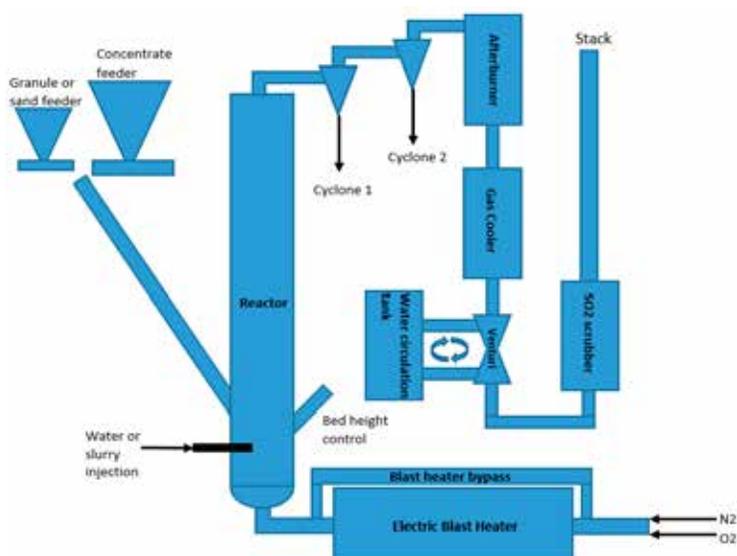


Fig. 1. Fluidized bed process schematics

Feeding system

Feeding is possible in three separate feeders. Two of them are screw feeders for powdered material and one smaller vibration feeder for granular material. They are gravimetrically controlled for exact control of the feed rate. For the first pilot campaign a slurry feeding system was created where the sulphur concentrate was mixed with water in an agitated tank and pumped into the bed part.

Gas cleaning

Immediately after the reactor the calcine is separated from the gas using two cyclones. The calcine ends up in two barrels where the primary barrel is continuously weighed. The gas passes through an afterburner where oxygen is added to eliminate any combustible material before the rest of the gas cleaning. The gas is cooled in a gas-gas heat exchanger before a venturi scrubber and finally a SO₂-scrubber before the stack. The ESP filter was not used during these tests.

Data collection

The system collect data every second and the different signals that is collected include: feed rates from all feeders and flow rates for all gas inputs, outgoing solid material weight, temperature and pressure throughout the system and gas analysis of O₂ and SO₂ post reactor.

Concentrate analysis

The typical moisture content of the sulphur sludge is 30 % but can vary between 20-40 % depending on the performance of the filter presses. The particles have a d₅₀ of 9.6 µm and a d₈₀ of 16.6 µm. The zinc concentrate have a d₅₀ of 22.5 µm and moisture content around 8 %. In Table 1, analysis of the two materials is presented.

Table 1. Sulphur sludge and zinc concentrate analysis.

Element	S	S(el) +S2-	SO4 -S	Fe	Zn	Pb	Ca	Si
By weight	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
Sulphur concentrate	67.9	65.1	2.6	9.0	4.1	1.1	0.48	1.20
Zinc concentrate	31.5	29.8	1.8	6.6	55.2	1.6	0.29	0.76

Method

Granulation

The granulation was performed with variable amounts of water in order to obtain non-sticky and mechanically stable granulates. The finished granules were characterized for stickiness, particle size, dry compression strength, abrasion and feeding test. An example of the finished the finished granulation product is presented in Fig. 2



Fig. 2. Granulated leaching sludge

Fluidized bed campaign no. 1

The day before the campaign starts, the fluidized bed reactor was pre heated using max input from the electric blast heater and a gas flow of 60-70 Nm³/h. The system was then closed for the night to maintain heat.

At start-up of the system 55 Nm³/h of pre-heated air was introduced at the bottom of the reactor. When the temperature in the reactor has reached the designated processing temperature the gas flow was decreased to allow for addition of bed sand. When temperature recovers from the sand addition the slurry pump was started and the slurry was carefully pumped into the reactor and allowed to ignite. When ignition was achieved the slurry flow rate and all other relevant parameters were guided towards the first test point of the day.

The roasting was carried out in the temperature range 700 – 750 °C.

At the end of each day the bed was cooled down to 300 °C by addition of water. After the bed has cooled down, a bottom plug was removed and the bed was emptied.

Table 2 presents the outcome of the different process parameters used during the first fluidized bed campaign. When changing regime, the temperatures were allowed to stabilize before starting any new sampling.

Table 2. Test regimes for campaign no. 1

Test Day	Test No	Residue rate	Sand rate	Blast rate	%O ₂ -blast-calc	T bed - aim	O ₂ -demand- Theoretical	O ₂ -coefficient- calc	% Water slurry	Slurry rate aim
		kg/h	kg/h	Nm ³ /h	vol-%	°C	Nm ³ /ton residue		wt-%	kg/h
Day 1	F23-F26	5.0-10.1	1.0	21.5-30.0	22.9-25.3	700-750	560	1.3-1.9	55	11.1-22.5
Day 2	F27-F33	5.0-18.0	2.0	15.9-35.7	21.0-30.2	750	568	0.8-2.2	50	10.0-36.0
Day 3	F34-F39	9.9	2.0	19.7-28.1	21.0-30.0	700-750	568	0.8-1.1	45	18.0
Day 4	F40-F44	9.9-16.5	2.0	21.4-44.6	21.0	750	568	0.8-1.0	45	18.0-30.0

Fluidized bed campaign no. 2

The day before the campaign begins the fluidized bed reactor was pre heated using max input from the electric blast heater and a gas flow of 60-70 Nm³/h. The system was closed for the night to maintain heat.

At start-up of the system 40 Nm³/h of pre-heated air was introduced at the bottom of the reactor. During heating the reactor was filled with 25 kg of calcine from the Kokkola zinc roaster as a starting bed. When the temperature reaches 890-900 °C, feeding of Zn-concentrate starts at a careful rate. When the bed ignites the temperature was regulated towards the target temperature for the first test regime using the partial bypass of the blast heater. Granule feeding can start after ignition has occurred.

The roasting was carried out in the temperature range 900 – 950 °C.

At the end of each day the bed was cooled down to 300 °C by addition of water. When the bed was cooled down, the bottom plug was removed and the bed was emptied. On the third and fourth day some tests using only S-sludge granules were performed. For safety reasons the bed was still filled with calcine to start with.

Feeding of material was done with two feeders, one screw feeder for zinc concentrate and a vibration feeder for granulated material. Two different granules were used: one granule type used only S-concentrate and the other type used an 80/20 mix of zinc concentrate/S-concentrate

Table 3 shows the outcome of the measured parameters during the second campaign. F62-F66 use 100% S-concentrate granules, the other tests use the 80% zinc concentrate to 20% S-concentrate mix.

When changing test regime, the temperatures were allowed to stabilize before starting any new sampling.

Table 3. Test regimes for campaign no. 2

Test day	Test No	Concentrate feed rate	Granule feed rate	Make- up water	Blast Rate	%O ₂ Blast	T Bed	O ₂ Demand	O ₂ Coefficient	% Moisture in feed (incl make-up)
		kg/h	kg/h	l/h	Nm ³ /h	vol- %	°C	Nm ³ O ₂ /Ton dry mix		wt-%
Day 1	F50-F54	6.8-9.9	6.2-8.2	0.58-0.70	30-36	21	900-950	378-504	1.05-1.40	7.1-7.9
Day 2	F55-F59	4.4-9.7	7.7-11.3	0.43-0.70	27-31	21	920-923	342-418	0.95-1.16	7.2-7.8
Day 3	F60-F63	0.0-3.5	9.4-14.4	0.24-3.46	28-30	21	772-932	444-666	1.16-1.24	8.3-40.9
Day 4	F64-F69	0.0-11.4	1.6-9.6	0.24-1.11	27-31	21	923-929	377-648	1.05-1.40	7.1-9.4

Results

Fluidized bed campaign no. 1

The sulphur content analysed by Leco-S shows that the sulphur content has little variation with oxygen coefficient >1.1, Fig. 3, below 1.1 Leco-S tend to be higher. Fig. 4 shows the temperature dependence on the Leco-S results where there is higher sulphur at lower temperature.

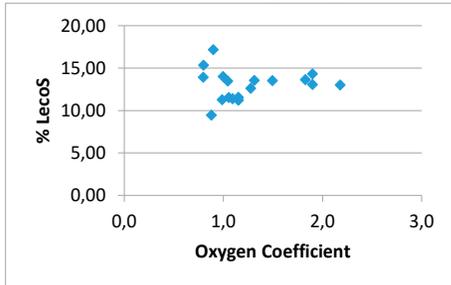


Fig. 3 Sulphur content of calcine with respect to the oxygen coefficient.

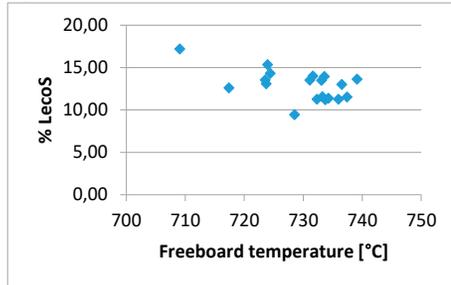


Fig. 4 Sulphur content of calcine with respect to the freeboard temperature.

Table 4 shows a qualitative XRD analysis of calcine samples, the quantitative results presented are not precise. The results include silicate material including quartz (Qz), plagioclase (Pl) and feldspar (Kfs) partly from the bed sand. The zinc containing materials are Sphalerite ((Zn,Fe)S), Zincosite (ZnSO₄), Willemite (Zn₂SiO₄), Franklinite (ZnFe₂O₄), Zincite ((Zn,Mn)O), and Bianchite ((Zn,Fe²⁺)(SO₄)•6(H₂O)).

Table 4. Mineral content % by XRD analysis of cyclone 1, campaign no.1

Nr.	LabID	Sample	Qz	Pl	Kfs	Sp	Hem	Zink	Wil	Mag	Frk	Zinc	Brt	Bia	Roz
1	S-1243	F24-C1-1	26	18	16	9	8	5	3	-	3	1	3	4	4
2	S-1246	F30-C1-1	26	14	16	9	9	5	4		3	3	3	4	4
3	S-1251	F37-C1-1	24	17	19	9	10		4		6	3	3	5	
4	S-1253	F39-C1-1	23	17	17	10	9		5	6	6	3	4		
5	S-1255	F40-C1-1	24	18	24	12	10		3		4	2	3		
6	S-1258	F42-C1-1	23	19	20	16	6		3	8		2	3		

Qz (Quartz), Pl (Plagioclase), Sp (Sphalerite), Hem (Hematite), Zink (Zincosite), Wil (Willemite), Mag (Magnetite), Frk (Franklinite), Zinc (Zincite), Brt (Baryte), Bia (Bianchite), Roz (Rozenite)

The combustion or removal of S is on average 94.2 % for the entire campaign, the individual tests are shown in Fig. 5.



Fig. 5 Combusted sulfur % during campaign no. 1

Fluidized bed campaign no. 2

Fig. 6 shows the remaining sulphur in the samples taken from cyclone 1. Interesting points are further explained in the figure. The last 2 samples during day 3 was an attempt to rapidly cool the process to the temperatures that was used during the first campaign, granules were roasted with no addition of concentrate for these test points.

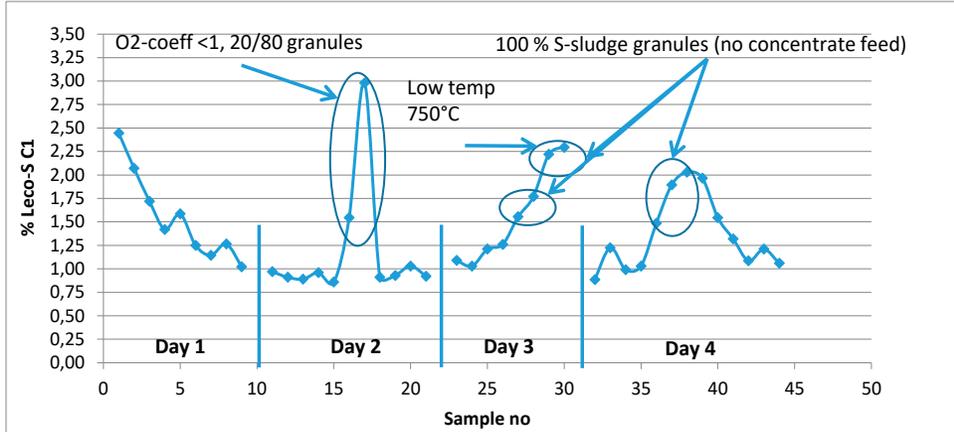


Fig. 6. Leco-S, all samples in order.

Fig. 7 shows for the experiments using 80/20 granules how the remaining sulphur in the calcine is dependent on the theoretical oxygen coefficient. The breaking point over which no significant change can be found is 1.1, but lowering the oxygen content below have a clear effect.

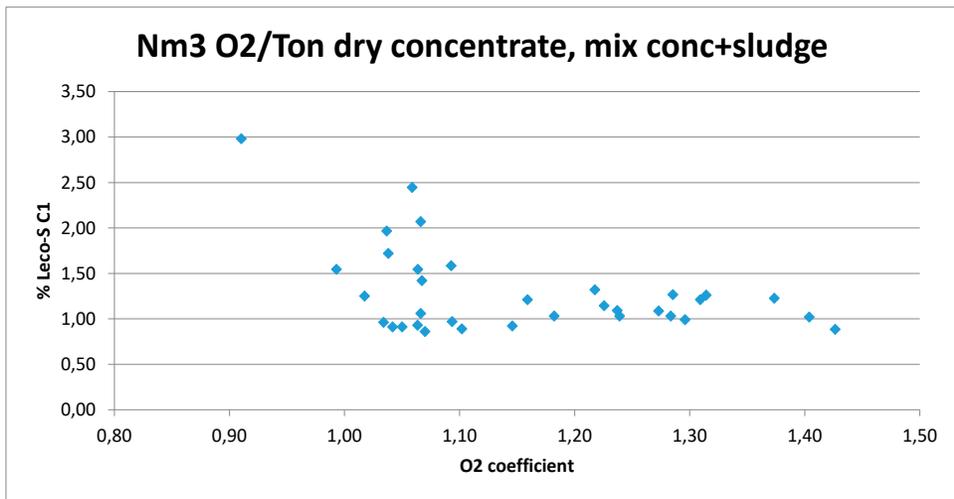


Fig. 7. Leco-S dependency on O₂ coefficient, mix granule and concentrate feed.

Fig. 8 shows, for the 100 % S granules, the dependence of remaining sulphur on the oxygen coefficient in the blast. Fig. 9 shows, for the 100 % S granules, the dependence of the remaining sulphur on the average global temperature in the reactor.

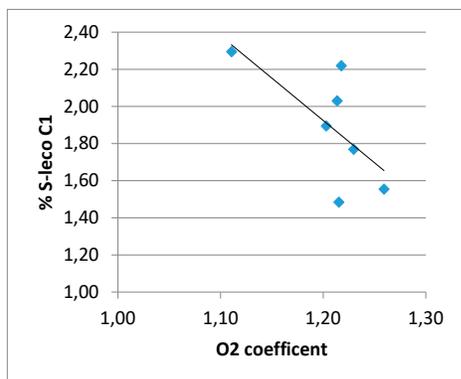


Fig. 8. Leco S with respect to O₂ coefficient, 100 % sulphur sludge.

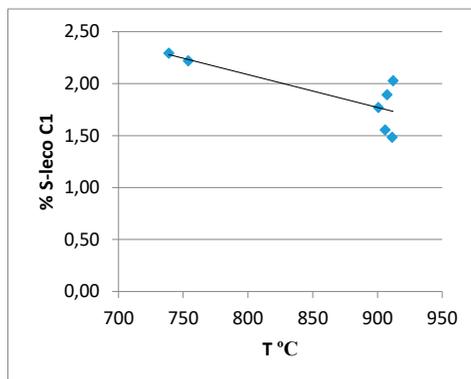


Fig. 9. Leco S with respect to global temperature, 100 % sulphur sludge.

Table 5 shows the qualitative XRD results of material sampled from cyclone 1. Test F62, F63 and F66 are used with only 100 % S-concentrate granules and have a mineral profile that is different from the rest.

Table 5. Mineral content % by XRD analysis of cyclone 1, campaign no. 2

Sample ID	ZnO Zinkite	(Zn, Fe ²⁺)Fe ³⁺ ₂ O ₄ Franklinite	Zn S Sphalerite	PbSO ₄ Anglesite	Zn ₂ SiO ₄ Willemite	Fe ₂ Pb(SO ₄) ₄ (OH) ₁₂ Plumbojarosite	SiO ₂ Quartz	Fe ₂ O ₃ Hematite	ZnSO ₄ ·6(H ₂ O) Bianchite
F50-C1-2	59	17	6	3	10	-	5	-	-
F51-C1-2	58	19	4	4	9	2	4	-	-
F52-C1-2	58	18	3	4	9	3	5	-	-
F53-C1-2	57	18	3	5	8	3	6	-	-
F54-C1-1	60	19	2	4	8	2	5	-	-
F55-C1-3	59	17	2	4	10	3	5	-	-
F56-C1-2	62	18	2	3	8	2	5	-	-
F57-C1-2	57	17	10	3	9	-	4	-	-
F58-C1-2	58	17	3	4	8	3	7	-	-
F59-C1-2	64	18	1	3	9	-	5	-	-
F60-C1-2	63	20	2	3	8	-	4	-	-
F61-C1-2	60	19	2	3	10	-	6	-	-
F62-C1-2	34	21	1	4	12	-	16	7	5
F63-C1-2	27	18	5	4	11	-	24	11	-
F64-C1-2	60	17	4	3	8	3	5	-	-
F65-C1-2	60	17	2	3	9	3	6	-	-
F66-C1-3	36	20	1	4	11	-	18	5	5
F67-C1-2	62	17	3	3	8	2	5	-	-
F68-C1-2	59	18	2	3	10	3	5	-	-
F59-C1-2b	61	18	3	3	8	2	5	-	-

Discussion

Fluidised bed campaign no. 1

It is clearly seen in Fig. 3 that the sulphur content of the samples have very low variation when the oxygen coefficient is above 1.1. By omitting these results for oxygen coefficients >1 render it possible to define the temperature dependence as shown in Fig. 4, where higher temperatures results in lower sulphur levels.

The high content of sulphur and especially elemental sulphur make it fairly straight forward to remove 94 % of the initial sulphur content during roasting. The remaining calcine is a small fraction of the mass of the fed sulphur concentrate making sampling a challenge. The small calcine mass flow also made the bed sand an analytical problem since the sand fraction in the cyclones was non-negligible. The high relative remainder of sulphur in the calcine (approximately 13 %) could be explained by slow kinetics and non-dissociated sulphates that is not dissociated at temperatures below 800 °C. Table 4 show that the calcine contains sulphates and even Sphalerite after roasting, for perspective normal roasting temperature for zinc concentrates is in excess of 900 °C.

Fluidized bed campaign no. 2

The campaign begun with a steady decreasing sulphur levels from 2.5 % to around 1 % which is evident from Fig. 6. The reason for this is believed to be that the system (which was cleaned before the campaign) has a hard time keeping a high temperature in the whole reactor. When more material is put through the system more material accumulates and acts as insulation.

What can be seen in Fig. 6 is that both tests using pure S-concentrate granules increase the sulphur content. During day three it is clear that the remaining sulphur in the calcine is increasing even before the temperature is lowered to 750 °C. During day 4, the increase of remaining S can be shown to start when the 100 % sulphur concentrate granule feeding starts. The sulphur content then decreases after the 100 % granules stop feeding, the decrease is slow due to some inertia in the system. This indicate that there is some sulphur containing species in the sulphur concentrate that is hard to oxidise or dissociate, one possible compound is CaSO₄ as the granules contain 0.5 % Ca before combustion.

The test with only S-granules at 750 °C was an attempt to replicate the first campaign. During the second campaign the highest achieved sulphur content was about 3 %, which is low compared to the 10-15 % reached in campaign no. 1. This test at 750 °C was quite short and it is probable that the inertia in the system hindered the results from reaching 10-15 %. It is also possible that the drier air in campaign no. 2 benefited the combustion of sulphur and achieved lower sulphur content due to higher partial pressure of oxygen.

The XRD results show that the samples using only S-concentrate granules contain significantly lower amounts of Zincite and higher amounts of quartz and hematite. Bianchite (ZnSO₄*6(H₂O)) decomposes at 125 °C, so the samples analysed to contain Bianchite either is wrongly analysed or came into contact with moisture after sampling.

Conclusions

- The combustion of sulphur was on average 94 % during the first campaign and 97 % during the second. There is no noticeable difference between feeding zinc concentrate and sulphur concentrate as a mixed granule or as separate material streams. Feeding sulphur concentrate as a slurry yields a lower combustion of sulphur.
- S-residue could be roasted as pure and also mixed with zinc concentrate.
- Roasting S-residue together with zinc concentrate was successful and promising for industrial scale application.
- The oxygen coefficient should be at least 1.1 or above for the remaining sulphur to be within an acceptable range in industrial scale.
- The temperature has a beneficial effect on the sulphur removal, but this is only clearly seen when the oxygen coefficient is very low.
- The average dry gas composition was 2.9 vol.-% O₂ and 11.1 vol.-% SO₂ during the second campaign, which is suitable for sulphuric acid production.
- Feeding the material as a slurry is the safest way of feeding, but already at 750 °C the process had an energy balance problem and was only able to function due to the added energy from the blast heater.
- The potential self-ignition of sulphur must be avoided; thus sufficient moisture level must be kept in the feed. Blending the sulphur concentrate with zinc concentrate achieves the same goal.