"DECOMPOSITION OF METAL SULFATES - A SO_2 -SOURCE FOR SULFURIC ACID PRODUCTION"

J Hammerschmidt and M Wrobel

Abstract and Introduction

The peak in Sulphur price late 2008 caused again intensified investigation into the decomposition of sulphates and spend acid. One option is the recycling of sulphur from spend acid, which already started more than 40 years ago in the field of spend acid from organic processes in refineries and acrylic glass manufacturing. Since this acid couldn't be neutralized and discarded due to high organic contents, another source of SO_2 to produce sulfuric acid is the decomposition of metal sulfates. The decomposition of metal sulfates was investigated at the next peak in Sulphur price in the 80's. The first major scale pilot tests and studies of gypsum decomposition were carried out for clients in Florida.

The decomposition of gypsum was quite often mainly influenced by the strategic decision of some countries to get own and independent acid production. In other cases the industry doesn't have enough space to dump the gypsum. Therefore the company was also forced to convert the gypsum into "saleable" products to avoid these residues. Other projects were made for the recycling of iron-sulfates from the pigment industry. The motivations for these projects were not only given by acid price. For the German pigment industry it was no longer permitted in the 80's to dump the iron sulphate residues into the sea. These regulations forced the industry to develop new technology, which allows converting of the $FeSO_4$-residues into iron oxide and acid. Therefore economical and mainly environmental factors influenced the decision of the companies to develop and to build these plants.

Beside the above mention iron- and calcium-sulphates many other process exist, which produce metal sulphates as an intermediate product. These cases are not forced by environmental or strategic factors. In cases like Ni, Co or Mn-decomposition the main product of the plant is treated in the decomposition plant and later on used as ferrous-alloys. These final products are higher in price compared to e.g. CaO, which exclude the high-energy consumption for the endothermic chemical decomposition reaction.

The reaction of SO_2 generation based on acid or sulfate decomposition takes place in the range of 1000°C. The energy demand of the endothermic reaction is considerable and leads due to the high fuel-combustion off-gas stream to a diluted SO_2 gas. Energy prices are usually increasing at the same time like sulphur. Sulphuric Acid based on decomposition is therefore more expensive than as acid based on sulphur combustion.

The paper describes fluid bed technology and possible process concepts for decomposition plants. Additionally the thermodynamic background of the decomposition process and the main influence factors are provided to receive a better understanding of this technology.

Potential index :

1 Fluid Bed Technology for Decomposition Plant

The decomposition of sulphates can be carried out in multiple-hearth furnaces, rotary kiln or fluidized bed furnaces with the addition of elemental sulphur, pyrite, coke, plastic, tar, lignite, hard coal or oil as the fuel compensator. Depending on the capacity and kind of metal sulfate these different technologies are in use today. Mainly older productions use multiple hearths or the kiln technology. For example the decomposition of gypsum is done according to the Müller Kühne Process in rotary kilns. Following table shows typical numbers of a formerly existed Müller Kühne decomposition plant in Industriepark Bitterfeld, Germany with two production lines.[1]

Feedmaterial:

- Raw material/Residues: 200.000 t/a,
- Old Acid: 20.000 t/a and
- Combustables: 40.000 t/a

Products:

- Cement: 100.000 - 130.000 t/a
- Sulfuric Acid: 70.000 - 100.000 t/a

For the decomposition of iron sulfate it is common practice to use fluidized bed reactors. Following table shows the Process of a typical iron sulfate decomposition plant:

Number of salt feed points	2
Bed cross section area	20 m²
Bed height	1.4 m
Temperature	800 - 900°C
Number of oil feed points	15 - 20
Fuel oil consumption	2 000 kg/h
Fluidizing air	13.000 Nm³/h
Cinders	4 t/h
Steam	8 t/h

The stationary fluidized bed is the conventional type of fluidized bed technology for the decomposition of metal sulfates and to recycle spent acid. This kind of operation is characterized by a low fluidizing velocity, a high particle density within the bed and a defined interface between bed and freeboard. The use of a cyclone for the separation of particles in the reactor off-gas depends on the application and is not always required. This classical system has found repeated use not only for decomposition, also for roasting sulphide ores and concentrates with the subsequent production of sulphuric acid and utility steam. Following Table shows a list of fluid bed reactors used for decomposition:

Table 1: Examples for decomposition Plants[2]

Company	Country/Town	Capacity t/day (100%-H2SO4)	Feedstock
Cincarna	Slovenija/Celje	235 t/day	Ferrous Sulphate, Pyrite
Tioxide	France/Calais	270 t/day	Ferrous Sulphates/ Coal
Röhm - Hüls	Germany/Wesseling	400 t/day	Spent Acids
Röhm - Hüls	Germany/Worms	650 t/day	Spent Acids
Sachtleben Chemie GmbH	Germany/Sachtleben	2000 t/day	Spent Acids; Sulphates Roasting
Kerr McGee	Germany/Krefeld	600 t/day	Spent Acids; $FeSO_4$, Pyrite
Lanxess	Germany/Leverkusen	435 t/day	Spent Acid

The maximum throughput of the fluidized bed reactors is limited by the size of the reactor bed. As usual the expected production capacities are increasing also in this area of technology. This fact resulted into the use of Circulating Fluid Bed-Technology (CFB). Typically for circulating fluid bed systems, the calcine produced in the reactor will be carried over with the gas into the recycling cyclone and will return to the CFB reactor, thus forming the so-called circulating fluid bed system. The operating temperature of the decomposition process can reach from 700 up to 1000°C. Unfortunately the efficiency of cyclones is decreasing with increasing temperature. Similar to other process like rotary kiln it's not possible to avoid the carry over completely. Thus some parts of the concentrate will be carried over together with the off-gas into the next process step. Due to the lower temperature in these steps after reactor some backformation to metal sulfates can occur. Depending on the final product quality regarding the sulfur concentration the carry over has to be recycled or can be mixed with the low sulfur-containing product from the reactor. But most of the solids are separated from the off-gas and are recycled through the seal pot into the main reactor and can be discharged through the below shown Product stream. The main structure of the common CFB is shown in Fig. 1

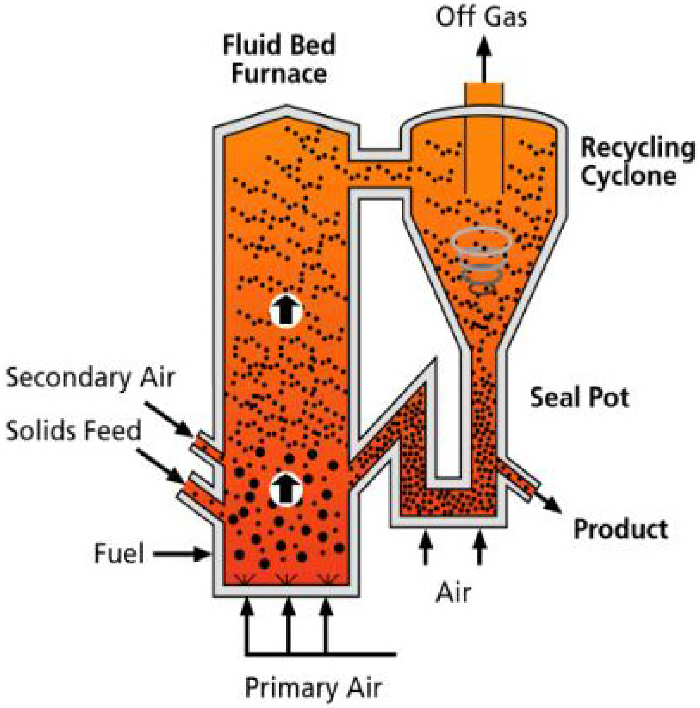

Fig. 1: Circulating Fluid Bed – Concept-drawing

The development of such CFB system started in the 1960's when the need for an efficient, compact calcination stage appeared in the bauxite industry. The use of the fluidized bed reactor as an alternative was considered but the small particle size feed would mean that low gas velocities be employed to maintain a well defined fluidized bed. Also, since large volumes of gas are to handle at the high temperature operation for the required reactions and heat transfer to take place, this would have meant the construction of large, difficult to control fluid bed reactors. The basis for further development work was thus laid and the first commercial Circulating Fluid Bed Reactor designed and installed by Lurgi, was commissioned during the 1970's for the calcining of aluminium hydroxide in Lünen, West Germany. With the inception of the Alumina Fluid Bed Calcination, as it was called, numerous applications evolved.

As of today there are 268 plants using the Outec's fluidized bed technology. The comparatively "younger" Outotec's -CFB technology is already used for 174 plants to date. These considerable number of Circulating Fluid Bed Systems, designed by Outotec are in operation or under construction worldwide for endothermic as well as exothermic processes. Some examples for these various applications are:

- The calcination of alumina hydroxide
- The calcination of gold ore
- The combustion of coal and lignite (power plants)

- The calcination of cement raw meal
- The combustion of wood and other materials and finally
- The oxidation of other Sulphide Concentrates etc.

Several parameters like throughput, feed material properties, retention time etc. affects the choice of the appropriate fluid bed technology. The typical features and major advantages of CFB systems in comparison with the conventional FB systems can be summarized as follows:

- Operation at high slip velocity, therefore, high specific throughputs and small unit sizes resulting in lower capital cost,
- Across the entire reactor system an improved control and uniformity of the operating temperature. Which ensures an uniform dead roasting of the material.
- Constant Gas condition/composition in the roaster system and its uniformity,
- Variation of solid residence time in a wider range, with the potential to improve dead roasting efficiency. This includes also the possibility to run with part load and load changes according to the concentrate composition.
- Suitability for exothermic and endothermic processes,
- Acceptance of feed material variations in chemical composition and particle size distribution ranges. Main limitations are the subsequent process steps like gas cleaning or sulphuric acid plant.
- Suitability to operate with highly oxygen enriched roasting air,
- Suitability for direct fuel injection like coal addition into the reactor,
- Reduction of heat losses.

The process advantages of the CFB system will increase with larger feed rates, as conventional Fluid Bed units lose on "homogeneity" with increasing roaster cross sections, whilst CFB systems still operate at comparably smaller reactor sizes of approximately only one tenth of the cross section. These features results in a high dead roasting efficiency and in view of the above-mentioned optimal roasting conditions for good operation conditions, the circulating fluid bed technology is the preferable process alternative to the conventional fluid bed technology for high process with high concentrate throughput.

2 R&D and scale up competence in Fluid Bed Technology[3]

Outotec's pursuit of new fluidized bed applications for customer needs is supported by experimental work in the company's in-house R&D Center. For example development of neural networks, in-situ monitoring systems and modern mathematical methods, including computational fluid dynamics modeling, are key elements of research.

Outotec has developed theoretical models of fluidized bed systems and specialist scale up know-how over many decades. A unique set of pilot plants, suitable for processing of feeds in the range of 100 g batches up to 1,000 kg/h continuously, is available to develop and improve existing technologies for customer applications. These pilot plants are designed to be flexible with respect to temperature, pressure, gas and fluidization conditions and can be configured either as single or multistage units. However, the data gained in laboratory scale fluidized bed systems are not sufficient to provide design and performance criteria of industrial plants without the experience of operating facilities.[4]

Outotec's largest test facility for this technology area at the R&D Center in Frankfurt is a 700 mm diameter CFB demonstration plant. This CFB is equipped with recycle cyclone, integrated heat generator, char separator, magnetic separator, gas cleaning system, and all necessary ancillary equipment. Additionally smaller CFB's like 300 and 200 mm diameter are installed at the R&D-centre.

For the design of new CFB plants, the data and process parameters developed for the new plant, such as particle size, fluidizing gas, gas velocity, etc., are compared with data from existing CFB operating plants in dimensionless units. The so-called Reh diagram illustrates the different phase behavior of gas-solids interactions based on dimensionless units (see Fig 2) The yellow region represents the fixed bed-operating domain. The blue region indicates the domain of the bubbling fluidized bed where gravity and drag forces on the particles are in balance. The gray section represents the pneumatic transport domain. The orange triangular region represents the area of the circulating fluidized bed. As the diagram is calculated for ideal spherical homogeneous particles it provides an indication only. However, coupled with experience from industrial plants the CFB operating range can be extended to area "a" of the diagram. This knowledge gained from operational experience is applied to the design of new plants and processes.

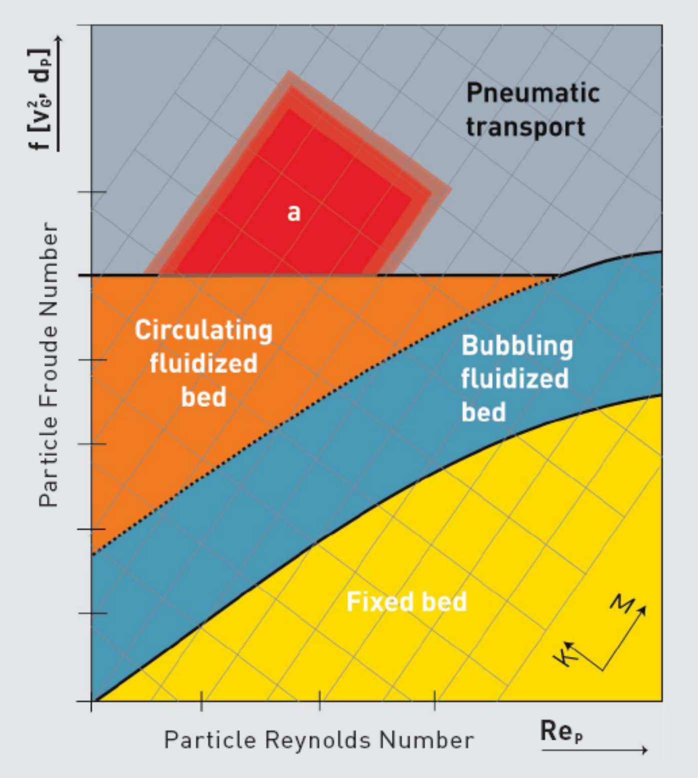

Fig. 2: Reh-Diagram

In course of time; Outotec has accumulated considerable knowledge and experience in developing scale-up criteria for plant design accruing from over fifty years of experience in engineering and supply of fluidized bed reactor plants starting from test work with the above mention pilot plants at its R&D-Center in Frankfurt. With Outotec's experience in many state-of-the-art fluidized bed technologies the customers do not need a large-scale demonstration plant as an expensive interim step. Following table shows examples of the scale up figures of former Outotec projects:

Process,	year	From pilot plant size	To industrial plant size	Scale up factor
Alumina calcination,	1970	D = 1,000 mm/24 t/d	D = 3,600 mm/500 t/d	1:20
Coal combustion,	1982	D = 360 mm/20 kg/h	D = 5,000 mm/500 t/d	1:1,000
Gold ore roasting,	1990	D = 200 mm/22 kg/h	D = 3,800 mm/2,000 t/d	1:4,000
Circored,	1999	D = 200 mm/18 kg/h	D = 5,000 mm/1,500 t/d	1:3,500

The following decomposition concepts were developed based on the above mention know-how.

3 Thermodynamic and Kinetic Background of the Metal sulfates Decomposition

The decomposition of metal sulphates is used in different chemical production routes. The best-known decomposition processes are the already mention treatment of iron sulphate to decompose the iron residues of the titanium pigment sulphate process and the decomposition of calcium sulphate to produce acid out of gypsum according to following equations:

$$FeSO_4 \rightarrow FeO + SO_3 \qquad \text{Equ. 1}$$

$$CaSO_4 \rightarrow CaO + SO_3 \qquad \text{Equ. 2}$$

The decomposition process is influenced by several factors the most important factors are:

- Temperature
- Atmosphere: Oxygen / CO/CO_2-Concentration
- Kind of metal oxide regarding affinity to form metal sulfates.(e.g. MnO, CaO)
- Kinetic - Retention time in the FB

The decomposition temperature cannot be clearly defined. Mostly, the term "decomposition temperature" means the temperature at which the partial pressure of SO_2 formed in the decomposition process reaches 1 bar. The influence of the temperature shall be demonstrated by the iron sulphate decomposition reaction in Fig. 3. This figure shows the thermodynamic equilibrium of the iron sulfate-decomposition reaction with high air/oxygen excess in the atmosphere. This specific decomposition of $Fe_2(SO_4)_3$ takes place in two steps. The first decomposing step of $Fe_2(SO_4)_3$ forms the intermediate product $FeSO_4$. The second step transforms the $FeSO_4$ to the expected final product Fe_2O_3. $Fe_2(SO_4)_3$ looses his stability already at 600°C. The decomposition of $FeSO_4$ starts afterwards at 750°C. Therefore the total decomposition of $Fe_2(SO_4)_3$ starts at 600°C and could be completed at approximately 1000°C. Between these two temperatures the conversion of iron sulphate to iron oxide increases and the final sulphur concentration of the solid product decreases.

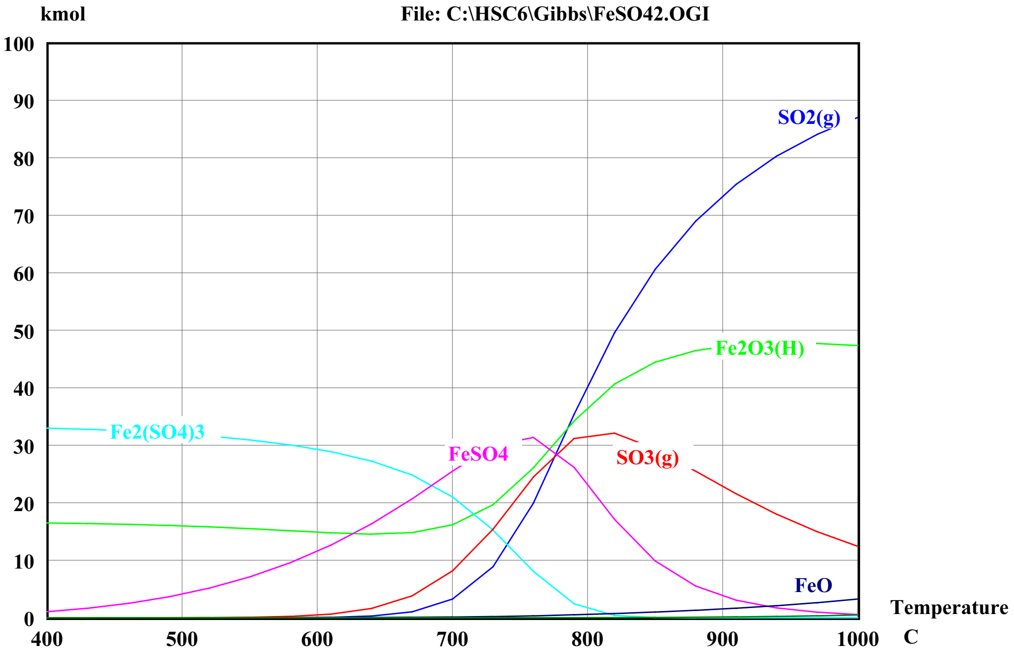

Fig. 3: $Fe_2(SO_4)_3$-Decompostion depending on temperature

Literature shows also some lower decomposition temperatures for iron sulphate decomposition. These temperatures are only possible under reducing atmosphere. The following diagram shall prove the influence of the atmosphere for the decomposition. On the two axes of the diagram the change of the partial pressures of O_2 and SO_2 are indicated. The chemical stability of any Iron sulphates composition increases with increasing SO_2-pressure and O_2-pressure. Oxidizing atmosphere in the reactor doesn't assist the decomposition reaction. The partial pressure of SO_2 in the reactor can't be changed too much. SO_2-gas is one of the products of the reaction and will always exist in higher concentration. Only the CFB can remove the SO_2/SO_3-gas very quick and supports the conversion of the metal sulphate. This effect will be described later. The oxygen gas is also one of the products, but can be consumed by side reaction like combustion of the fuels. Therefore the parameters that can be manipulated are SO_2/SO_3- and O_2-concentration and as previous already shown the temperature in the reactor can be changed according to fuel addition.

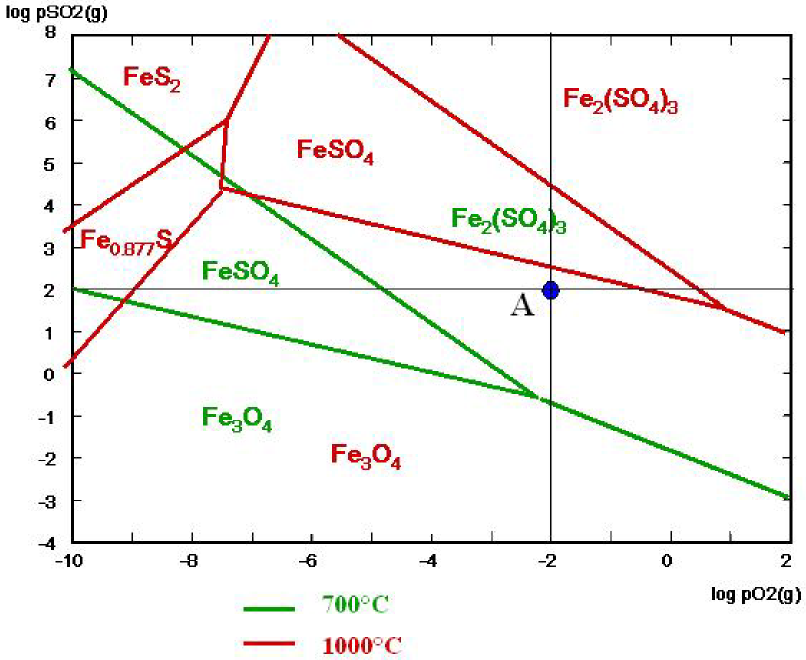

Fig. 4: Influence of the atmosphere and temperature on Fe2(SO4)3-Decompostion

The change of the operating temperature is shown in Fig. 4. At temperature of 1000°C (red lines) it's still possible to decompose iron sulphate even with high O_2 and acceptable SO_2-concentration in the atmosphere (see point A: $\log p_{O2} = -2$/ $\log p_{SO2} = 2$). At the same atmosphere and lower temperature the iron sulphate would be still stable and would not be decomposed. These changes on the $CaSO_4$-decomposition conditions depending on atmosphere and temperature are also shown on the Fig. 5. The decomposition line is parallel moving step-by-step down with increasing temperature.

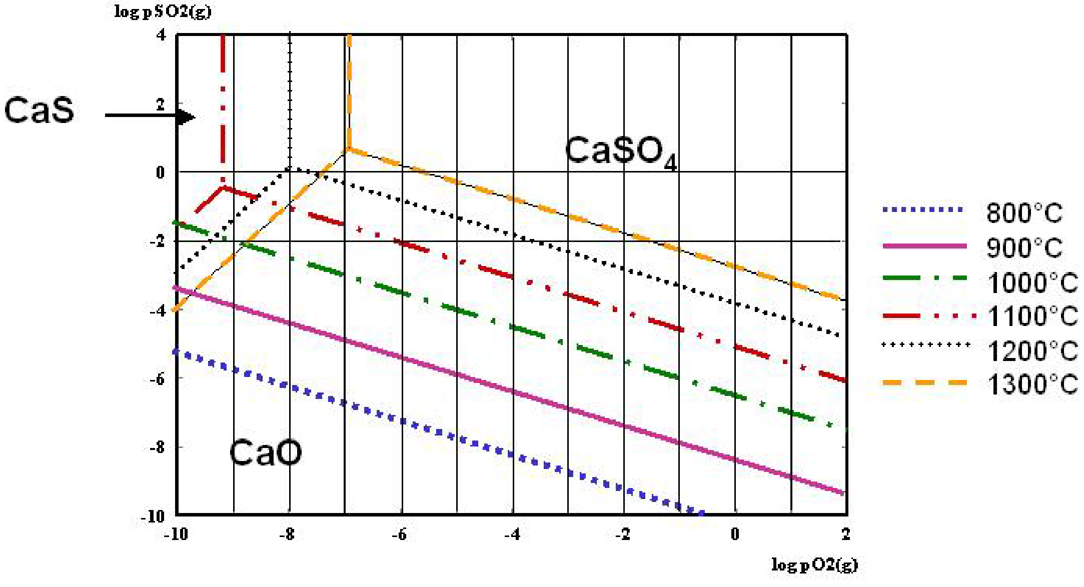

Fig. 5: $CaSO_4$-Decompostion depending on temperature

The final product quality does not only depend on the main metal-sulphate. Quite often the kind of minor concentration of other metal sulphates feed material is much more affecting the final sulphur concentration (see Fig. 6). The stability of metal-sulphates is very different. Most stable metal-sulphate is $CaSO_4$. Due to the high stability of $CaSO_4$ it is recommendable to decompose this compound in a kiln according to the Müller Kühne Process instead of using the fluid bed reactors. Unfortunately the throughput of a rotary kiln is very much limited. The previously shown example of the two Müller Kühne Plants in Bitterfeld shows the reduced capacity of a one kiln.[1] The next figure illustrates the different stability of metal-sulphates depending on atmospheric conditions at 850°C.

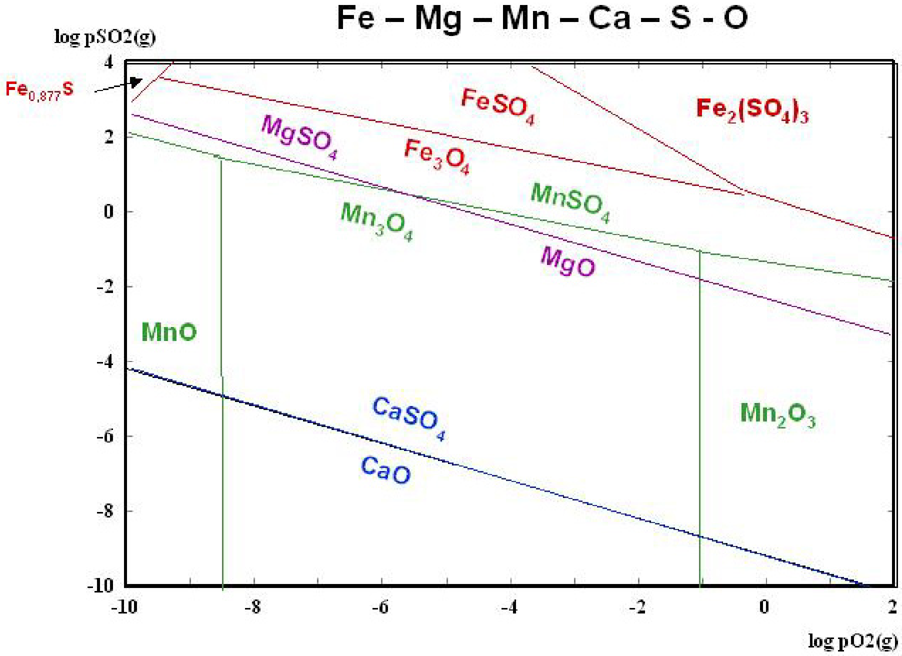

Fig. 6: Phase Stability-Diagram of X-SO_4-Decomposition at 850°C

Important for the decision of the right process equipment is, beside the thermodynamic parameters, the throughput and therefore the kinetic. The decomposition of sulphates is a dynamic process. The kinetic is affected by many factors. The most important are:

- The specific surface of sulphate grain
- The gas composition (atmosphere)
- The gas flow at sulphate surface

The Fig. 7 shows the simplified view of sulphate grain during the decomposition process in the fluid bed.

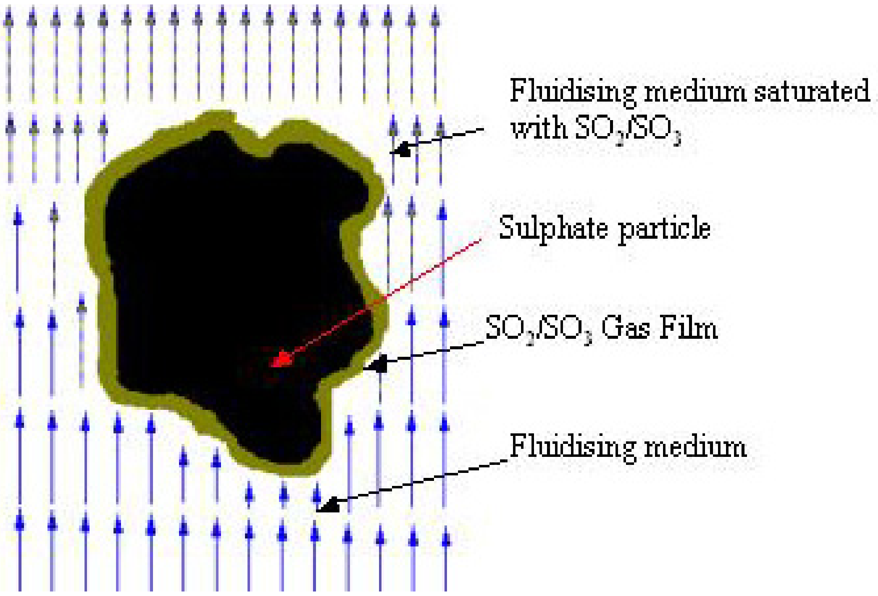

Fig. 7: Sulphate Grain during the decomposition process

During the decomposition of sulphates, a thin gas film is formed at the particle surface. The volume of this film is proportional to the particle surface and the partial pressure of formed gases. According to the chemical reaction and stoichiometric coefficients the partial pressure can be calculated.

$$2MeSO_4 \dashrightarrow 2MeO + 2SO_2 + O_2 \qquad \text{Equ. 3}$$

$$K_p = p^2_{SO2} \cdot p_{O2} \qquad \text{Equ. 4}$$

$$p_{O2} = 0{,}5p_{SO2} \qquad \text{Equ. 5}$$

$$p_{SO2} = (2K)^{1{,}5} \qquad \text{Equ. 6}$$

In this case, the decomposition in air is possible, if the partial pressure of oxygen formed in the reaction is greater than 0.21 bar. The above shown decomposition reaction can also be separated into tow steps. In the first step SO_3 in formed, which is in the second step transformed into SO_2 and O_2.

$$MeSO_4 \rightarrow MeO + SO_3 \qquad \text{Equ. 7}$$

$$SO_3 \leftrightarrow SO_2 + \tfrac{1}{2} O_2 \qquad \text{Equ. 8}$$

$$K_p = p_{SO3} \qquad \text{Equ. 9}$$

$$K_p = (p_{SO2} \cdot p_{O2}) / p_{SO3} \qquad \text{Equ. 10}$$

In this case, the decomposition is only marginal affected by the partial pressure of oxygen at particle surface. The part of oxygen formed during the sulphate decomposition can be consumed in the oxidation process or other side reaction in the reactor.

$$MeO + \tfrac{1}{2} O_2 \rightarrow Me_2O_3 \qquad \text{Equ. 11}$$

$$CO + \tfrac{1}{2} O_2 \rightarrow CO_2 \qquad \text{Equ. 12}$$

In reducing atmosphere the oxidation reaction of the metal oxides would be suppressed. It means, that without highly reductive atmosphere, the formation at low metal oxides is not possible.

In order to accelerate the decomposition reaction and to "increase the kinetic", the gas products must be removed from the particle surface. Only then, the next part of sulfate can be decomposed. The particle-surrounding atmosphere can be saturated only to the equilibrium partial pressure and that's why the decomposition process needs relative high temperature rather than retention times.

In case of decomposition in the fluid bed or circulating fluid bed the particles are almost ideally distributed in the gas phase. During the decomposition a part of the gas is continuously exchanged and due to very good contact with the gas phase, the formed SO_2/SO_3 can be easily removed from the particle surface. High turbulence and slip velocity between particle and gas phases supports the removal of the SO_2/SO_3-gas. The CFB is operating at the highest slip velocity and enables homogeneous temperature distribution and supports the removal of SO_2/SO_3-gas from the particle surface (see Fig. 8).

The interconnection of the decomposition rate from the slip velocity can be illustrated by the thermo gravimetric analysis. In our test we analyzed the decomposition rate of $MnSO_4$ particles with different N_2-flushing. The red lined used 200 ml/min of N_2-gas and the blue line only 20 ml/min. The used sample was about 36 mg and the used heating rate was 10 K/min. The weight loss of 44.135 % indicates, that Manganese oxide exist predominant as Mn_3O_4 (theoretical mass change –44.21%). This means that part of oxygen formed in the decomposition reaction oxidized the MnO. In case of high flow, the retention time was shorter of about 102 seconds.

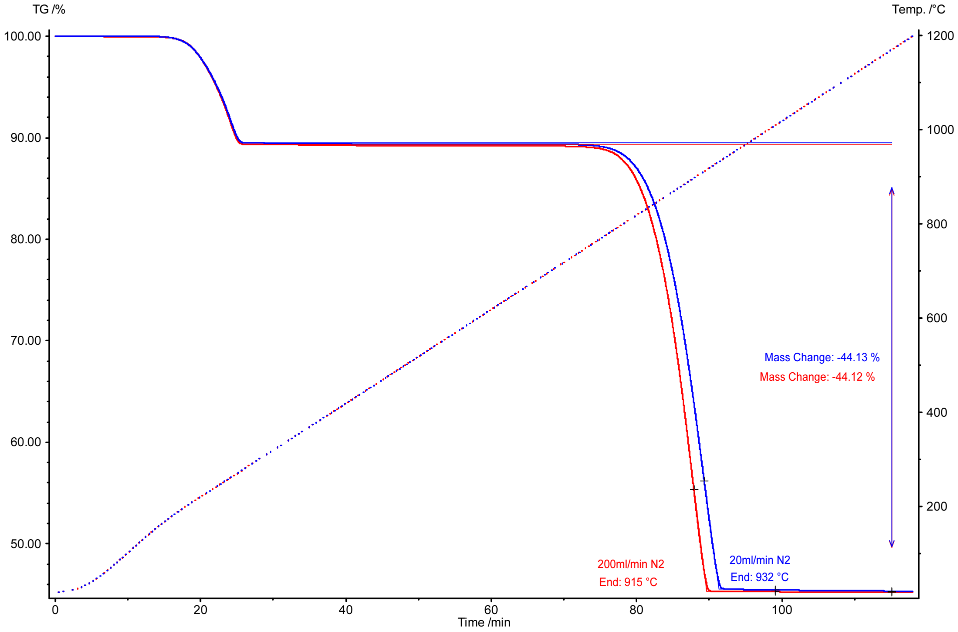

Fig. 8: Decomposition of $MnSO_4 \cdot H_2O$ in N_2 at different N_2- Flow.

The next figure shows the influence of oxygen on decomposition of $MnSO_4 \cdot H_2O$. It can be observed that in this case, the decomposition in the air starts and ends at higher temperatures and the retention time extends too 144 seconds. However the end product of decomposition - Mn_3O_4 is the same.

Summarized, the kinetic of decomposition can be affected by many factors. To produce oxides at low oxidations states, the highly reductive atmosphere is needed. In another case, the in the decomposition process formed oxygen will oxidize the metal oxide. The increasing of gas flow accelerates the decomposition process, reduces the required retention time and increases the throughput in the reactor. If the sulphate particles are physically feasible for fluidization and the thermodynamic stability is not as high as $CaSO_4$, than the fluid bed technology is the best solution for the decomposition process.

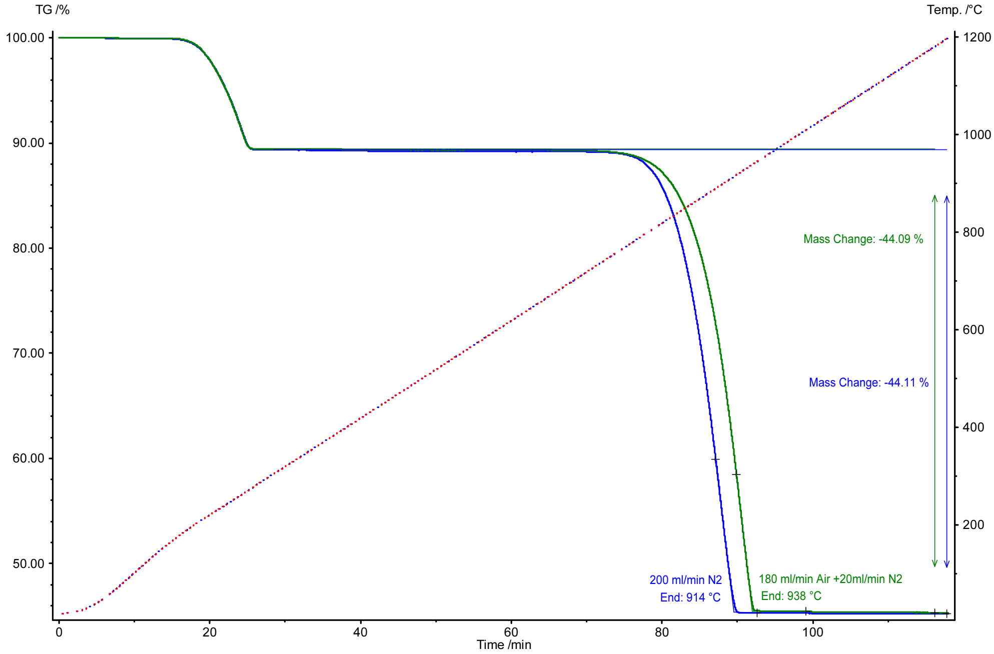

Fig. 9: Decomposition of $MnSO_4 \cdot H_2O$ in N_2 at different atmospheres
(blue 200 ml/min N_2; green 180 ml/min air + 20 ml/min N_2)

4 Process Concepts for decomposition of Metal-Sulphates[5]

In test work with iron sulfate and other metal sulfates a decomposition temperature in the range of 700 - 1000°C was found most suitable to achieve low sulphur concentration in the product. The decomposition of metal sulphates is strictly endothermic reaction and a considerable amount of heat is needed during the process in the CFB system. Additionally to the decomposition also huge amount of energy is needed for the remove of crystal water and surface water of the feed material if these water compounds are not removed before. Therefore, coal, LPG, Diesel or natural gas has to be added to the CFB reactor to control decomposition temperature at set point.

Today one of the most discussed topics in the word is energy recovery and saving in all areas of human life and technologies. Outotec is a well-known company, which always considers this aspect very eagerly in their technologies. The enormous energy requirement for the decomposition forces us to develop process modification and optimization for reducing the energy losses.

The second motivations for modification of the standard CFB-process is the above mention carry over of some solids in the next process steps. The solids that are carried over into the gas cleaning section could form metal sulfates again due to the lower temperature, high retention time and high oxygen concentration.

Any energy saving in this concept is equal to reducing the fuel addition into the roaster by recovering the energy from the hot discharges off-gas or calcine. For the internal energy recycling in the CFB-plant the energy in the off gas and product stream can be used.

Two different concepts are thinkable to recover the energy from the off-gas. The first concept is to transform the energy to the fluidization air, while the second concepts uses the off-gas energy to dry the wet feed material before feeding the material into the CFB. Both concepts are described in the following clauses. From the product stream the energy can be recovered by using a fluid bed cooler. This option can be found in all alumina calcining processes of Outotec.

The first concept recycles the energy to the fluidization air in the air pre-heater (recuperator). Similar to the second concept the process starts with the CFB plant including the cyclone and continuous with the air pre-heater (recuperator). The off-gas is cooled down in the air pre-heater while the fluidization air is heated up. The simplified arrangement of the process steps and description of the mass flows is shown in the following block diagram.

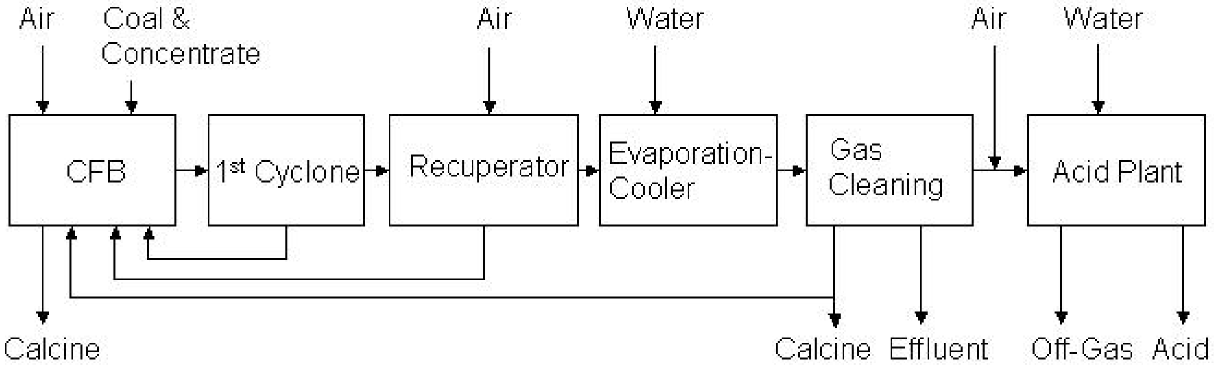

Fig. 10: Block Diagram – First Concept using an Air Pre-heater (Recuperator)

The second concept is shown in Fig. 11. The main difference to the fist option is the use of the Venturi Dryer combined with the 2nd cyclone instead of the air pre heater. The feed material is charged into the venturi dryer. The counter current entering off-gas from the CFB-plant dries the concentrate. The dried concentrate is carried over together with the off-gas into the 2nd cyclone. The cyclone separates the most of the concentrate from the off-gas. The concentrate goes over into the CFB, while the off-gas is sent to the evaporation cooler. The evaporation cooler assures in both concepts a constant temperature in front of the Hot Electrostatic Precipitation (1st step of the Gas Cleaning). In the Hot ESP the solid particles from the off gas are precipitated and recycled into the CFB. This concept is mainly for concentrate with high surface or crystal water feasible. In the venture-dryer this water can be removed before the solids enters the reactor. The following drawing shows the main process steps and the flows of the concept.

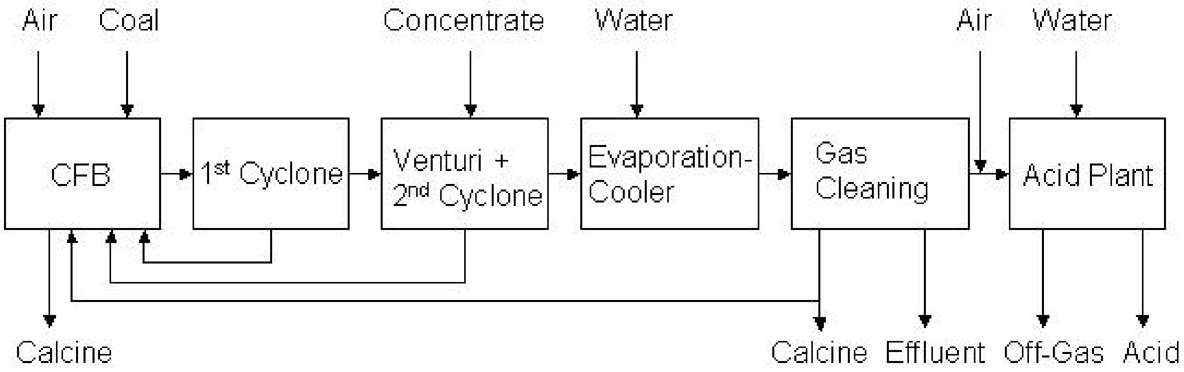

Fig. 11: Block Diagram - Second Concept with Venturi Dryer

With both concepts the fuel consumption in the CFB will be reduced compared to a plant without any energy recovery. The reduced fuel consumption causes the decrease of the off-gas volume stream and increases the SO_2-concentration in the off-gas stream.

5 Conclusion

Lurgi Metallurgie GmbH, since 2002 part of Outotec and recently renamed to Outotec GmbH, has progressively developed the principle of different fluidised bed reactor systems over a period of almost fifty years for a multitude of process applications. Its versatility has manifested itself in the treatment of minerals including solid fuels and for metallurgical processes both in the ferrous and non-ferrous fields. Process applications have ranged from acid plant, gas cleaning, roasting, plants, calcining, combustion and charring of coals as well as for decomposition of metal sulfates. This paper scrutinizes the thermodynamic, kinetic and process condition of the decomposition reaction.

The most critical influence factors for thermodynamic reaction of decomposing metal sulfates are the temperature and the atmosphere in the fluid bed reactor. For good results high temperatures and low SO_2 and O_2-concentration are beneficially. $CaSO_4$ are much more chemical stable even at higher temperature than $FeSO_4$ or $MnSO_4$. To decompose $CaSO_4$ very high temperature and low O_2 and SO_2-concentration is needed. Best results would be received with reducing atmosphere. Therefore $CaSO_4$ is the only metal sulfate, which should be decomposed in kilns. Unfortunately the throughput of kilns is more limited than in fluid bed reactors and the energy consumption are higher. In such high energy consuming process is this fact very important for the operating costs. Due of the nature of process condition of a rotary kiln solid fuel or reluctant is required. Very often coal or coke is used as fuel. The ash content of the coal/coke implies a certain amount of impurities in the solid decomposed product. The Fluid Bed technology enables also liquid of gas as fuel, which causes low impurities for the final product.

The kinetic in fluid bed reactor is much better than in kiln due to the high gas turbulence and efficient removal of SO_2-gas from the surface of the decomposed particles. This decreases the retention time and increases the throughput in the fluid bed reactor. Further increasing of the throughput can be reached by using a circulating fluid bed reactor instead of stationary fluid bed reactor.

The last part of our paper describes two suitable concepts, which are efficient and flexible to operate according to the requirements from raw material with regard to water and sulphur content. Main difference between the two concepts is the replacement of the air pre-heater by the venturi dryer with a second cyclone. With our concepts we are able to fulfill the low sulphur calcine concentration and some additional conditions. The main criteria of our first concept including the air pre-heater are:

- Energy Recovery from the Off-Gas stream in the air pre-heater.
- Direct energy recovery in the air pre-heater and reducing the coal consumption in the CFB
- Reducing of the off-gas volume stream and decreasing of the equipment size.
- Increasing the SO_2-concentration in the off-gas.
- High flexibility in the concentrate composition.

The main criteria's of this concept based in the venturi dryer are:

- Energy recovery from the Off-Gas stream in the venturi dryer.
- Saving fuel consumption for drying the wet concentrate before entering the plant.
- Reducing the volume of the off-gas stream and increasing the SO_2-concentration in the off-gas stream
- High flexibility in the concentrate composition.

6 Literature

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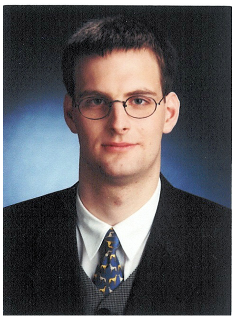
The Author



Jörg Hammerschmidt, Outotec GmbH, Product Manager – Pyro-/Hydrometallurgy

Jörg Hammerschmidt studied mechanical engineering/process engineering at the RWTH Technical University of Aachen. From 1998 too 2002, he worked as a scientific assistant at IME Process Metallurgy and Metal Recycling, RWTH Aachen. In 2003 he defended his Ph.D. thesis titled "Development of a new Process Route to produce γ-TiAl with Aluminothermic Reduction and Electro Slag Remelting". In January 2003 he started his professional career at Outotec GmbH (former Lurgi Metallurgie) as Process Engineer for non-ferrous technologies. He participated in different projects in the