Topsoe WSA Technology for New Polimetallical Acid Plant, Vmetais, Juiz de Fora

An Economic and Flexible Process to Treat Streams with Varying Concentration of SO_2

Paper presented at Cobras 2007

by

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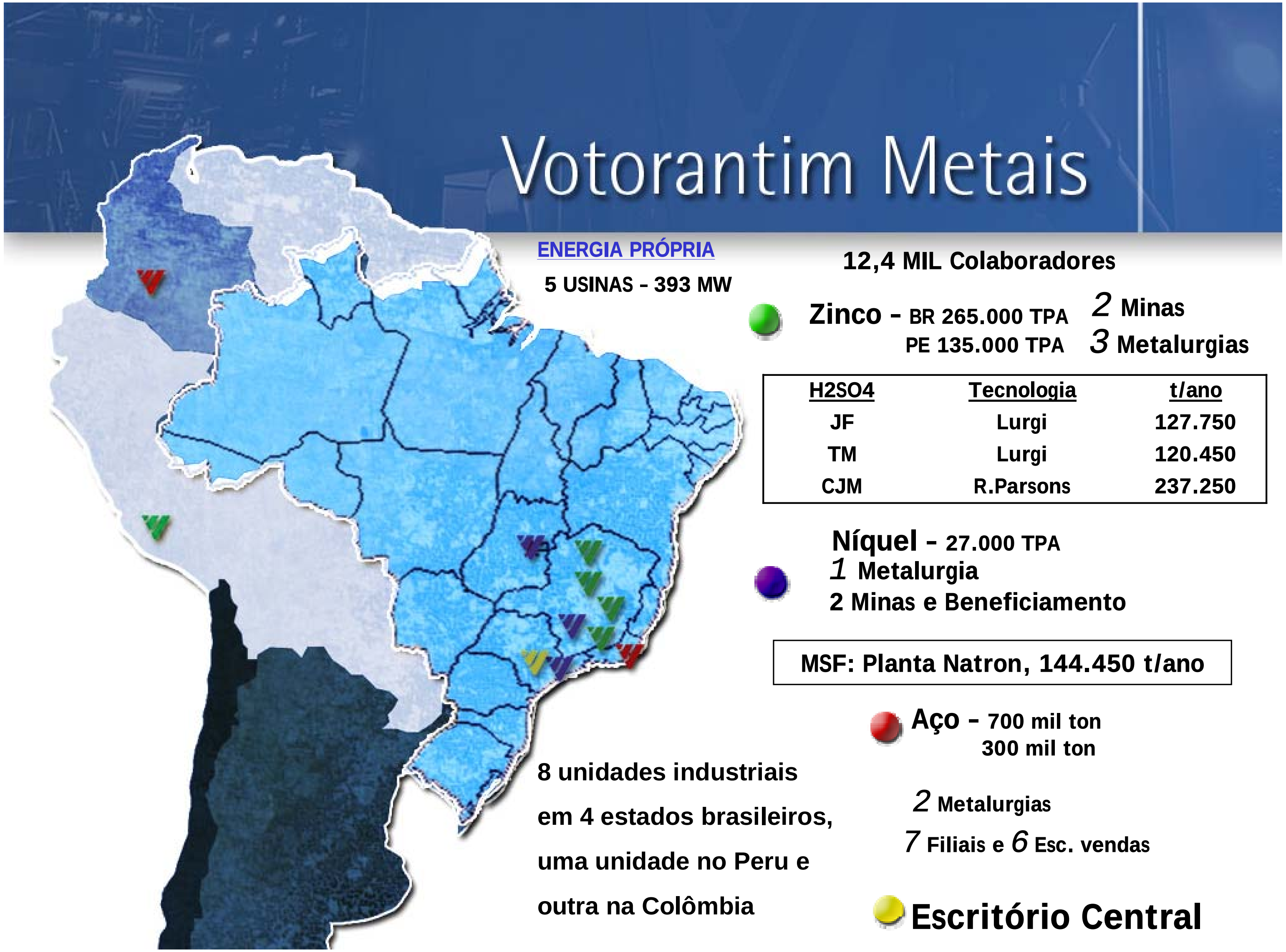
O Grupo Votorantim

- Fundado em 1918
- Um dos maiores grupos industriais do Brasil
- 8 áreas de negócios: metais, cimentos, celulose e papel, química, energia, agroindústria, finanças e novos negócios
- 50 mil colaboradores
- Unidades produtivas para o Exterior: Peru, Colômbia, Canadá e Estados Unidos
- Faturamento em 2006: R$ 29 bilhões

Em 2005, o Grupo Votorantim foi eleito pelo *IMD Bussiness School e Lombard Odier Darier Hentsch Bank* como a melhor empresa familiar do mundo

Votorantim Metais

- Entre os 10 maiores produtores mundiais de zinco
- Maior produtor de zinco na América Latina
- 3º maior produtor brasileiro de aços longos
- Produção integrada
- Geração própria de grande parte da energia consumida
- Vantagem competitiva no abastecimento de minério
- Gestão e competitividade nas suas operações


Votorantim Metais
ENERGIA PRÓPRIA
5 USINAS - 393 MW
12,4 MIL Colaboradores
Zinco - BR 265.000 TPA
PE 135.000 TPA
2 Minas
3 Metalurgias
H2SO4 Tecnologia t/ano
JF Lurgi 127.750
TM Lurgi 120.450
CJM R.Parsons 237.250
Níquel - 27.000 TPA
1 Metalurgia
2 Minas e Beneficiamento
MSF: Planta Natron, 144.450 t/ano
Aço - 700 mil ton
300 mil ton
2 Metalurgias
7 Filiais e 6 Esc. vendas
Escritório Central
8 unidades industriais
em 4 estados brasileiros,
uma unidade no Peru e
outra na Colômbia

Unidade Juiz de Fora

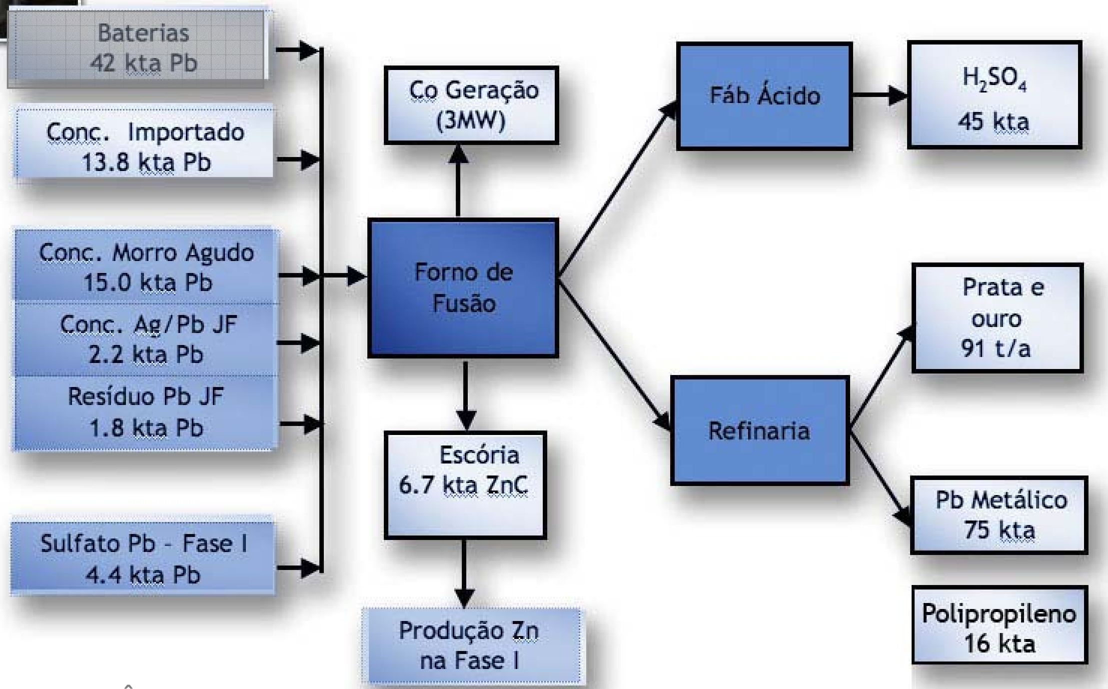
Linha do tempo

- **2002** Aquisição da empresa pelo Grupo Votorantim
- **2004** Produção de 95 mil t/ano de zinco
- **2005/2006** Produção de 98 mil t/ano de zinco
- **2007** Início do Projeto Polimetálicos

- 600 (próprios e parceiros fixos) e 440 (parceiros)
- Maior produtora e fornecedora de Pó de Zinco para pilhas no Brasil
- Única produtora de cádmio no país
- Maior produtora e única empresa que produz dióxido de enxofre para venda
- Melhor performance do mundo na operação do Ustulador
- Produz grande parte da energia consumida com as Hidrelétricas de Sobragi (Belmiro Braga) e Picada (Torreões)

Projeto Polimetálicos

O projeto otimiza sinergias em Juiz de Fora



Criação de valor com aproveitamento de resíduos e produtos agregados com práticas ambientais e ocupacionais seguras

Projeto Polimetálicos

Características do Projeto

- O processo TSL gera grande variação no teor de SO_2 do Off-gas ao longo de seu ciclo:

– Smelting:	6,5 horas:	9,8% de SO_2
– Redução:	1,0 hora:	1,5% de SO_2
– Vazamento da Escória:	0,5 horas:	0% de SO_2

- Performance Ambiental (D.N. 11 do Copam,16/12/1986):
  - Máximo de 2 kg/t de H_2SO_4
  - Névoa: máximo de 0,075 kg/t de H_2SO_4 e 10% opacidade visível.

- Planta Lurgi existente já passou por diversos “desengargalamentos” e não possui mais capacidade ociosa.

- Disponibilidade de SO_2 Líquido em outros processos da planta

Projeto Polimetálicos

Tecnologias Estudadas

- WSA - Wet Sulfuric Acid (Haldor Topsoe)
- Plantas Convencionais com Processo Seco
- Cansolv – Absorção de SO_2

Projeto Polimetálicos

Quesitos Analisados

- Aplicabilidade
- Capex
- Opex
- Manutenabilidade
- Disponibilidade Operacional
- Experiência da Tecnologia em Processos Semelhantes

Projeto Polimetálicos

Atividades Realizadas

- Visitas a Plantas Existentes
- Entrevistas com Usuários

Projeto Polimetálicos

Seleção de Tecnologia

Selecionou-se a Tecnologia WSA da Haldor Topsoe por:

- Flexibilidade de Processo (Turn down até 25%)
- Capacidade de operar com baixa % de SO_2
- Custo Operacional
- Confiabilidade
- Menor Investimento entre as Opções Disponíveis
- Referências

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An Economic and Flexible Process to Treat Streams with Varying Concentration of SO_2

1. Introduction

Today, quite a number of technologies are available to reduce the emissions of SO_2 generated by the metallurgical industry, each being suitable for its specific range of operating conditions. The Topsoe Wet gas Sulphuric Acid (WSA) technology is one of these technologies, particularly applicable for low- to medium-concentration SO_2 gases and medium gas flows. The WSA technology has demonstrated its superiority when it comes to total lifetime cost, taking not only the low investment cost, but also the attractive operating economy into consideration. Further the process has demonstrated its capability to handle SO_2 streams varying both in off-gas flow as well as in SO_2 concentration.

This paper describes the Topsoe WSA technology which was developed and commercialized during the early 1980s. The original intention was to make a cost effective technology available to the industry for removal of sulphur compounds from modest gas flows having only a low content of sulphur. Such lean gases are produced in a variety of industries and were to a large extent vented to the atmosphere. Due to new and expected future environmental legislation and regulations, there was in that period an emerging demand for technologies capable of treating this type of gases without prohibitively high investment and operating costs.

History has proven, however, that the range of applications for the WSA technology is much wider than originally anticipated. Today, 65 units have been contracted for gas flows ranging from 2,600 Nm^3/h to 1,000,000 Nm^3/h, and with daily sulphuric acid production ranging from 4 MTPD to 1,140 MTPD. Today the total acid capacity of WSA plants exceeds 11,000 MTPD. The WSA technology has found application in a variety of industries, viz:

- In the oil refining industry for treatment of amine regenerator and sour water stripper off-gases and for regeneration of spent alkylation acid.
- In the non-ferrous metallurgical industry for treatment of SO_2 containing off-gases from a variety of process units.
- In the petrochemical industry for treatment of acid gases from synthesis gas preparation units after oil and coal gasifiers.

- In the coke and coke chemical industry for treatment of acid gas streams from coke gas purification units and sulphurous gaseous and liquid streams from e.g. BTX rectification.
- In the viscose fibre industry for treatment of hydrogen sulphide and carbon disulphide containing off-gases.

2. Fundamental Principles of the WSA Process

The fundamental principles of the WSA process is shown in block diagram, figure 1, and described below.

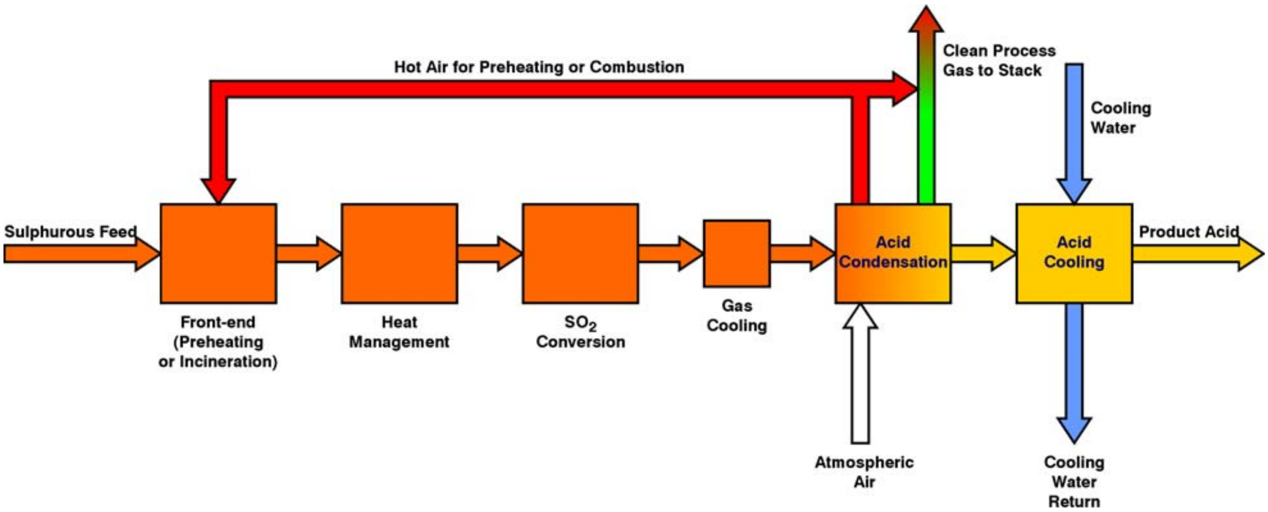

Fig. 1 - Principles of the WSA Process

The block diagram applies both for the case when the sulphurous feed is received as a **combustible compound**, such as elemental **molten sulphur** or **hydrogen sulphide gas**, or as an **SO_2 rich gas** coming from a metallurgical smelter or roaster. The name ***W**et gas **S**ulphuric **A**cid* was given to the Topsoe acid technology in order to emphasize that the concentrated acid is produced by condensation from a wet process gas. In consequence of this, the need for drying of the process feed gas prior to further processing is eliminated.

The process lay-out of the front end and the heat management system depends on whether the sulphurous feed is received in a form that needs incineration in order to oxidize the sulphur compound to sulphur dioxide, or the sulphur content already is on sulphur dioxide form.

Sulphurous Feed on Sulphur Dioxide Form
Sulphur dioxide containing gases generated in the metallurgical industry varies greatly, both with respect to gas flow and to sulphur dioxide concentration, all depending on the processes upstream the SO_2 fixation plant. If the SO_2 fixation unit is based on a catalytic SO_2 oxidation process, the gas must in any event be pretreated in order to remove particulate matters and catalyst poison, such as arsenic, down to levels acceptable to the SO_2 oxidation catalyst. Such gas pre-treatment systems typically consist of quench cooler, scrubbing unit, cooling tower and wet electrostatic precipitator. The feed gas to the WSA plant will in this case therefore usually be saturated, i.e. typically at the temperature of 30-40ºC and with a water content of approximately 6-7%.

The air, which has been used for cooling in the WSA condenser, will be available at a temperature of typically 210-220ºC and in sufficient quantities to preheat the SO_2 feed gas to approximately 150ºC. Further preheat of the process gas to the operating temperature of the SO_2 conversion catalyst of approximately 410ºC takes place in the heat management system, using the heat generated in the SO_2 conversion reactor.

After the preheating, the process consists of the following process units:

- SO_2 conversion
- Acid condensation
- Acid cooling

SO_2 Conversion
The catalytic SO_2 conversion process in a WSA plant is similar to the SO_2 conversion in a conventional acid plant based on absorption, except that the catalytic reaction takes place in a wet gas. Wet SO_2 oxidation catalysis has been practiced for decades, and Topsoe has developed special SO_2 oxidation catalysts of the VK-series for dedicated operation in wet gases.

The design of the SO_2 converter depends on the SO_2 concentration in the process gas and on the required degree of SO_2, conversion, i.e. degree of SO_2 removal, and features one, two or three catalyst beds. In case of a multi bed concept, interbed cooling is required.

Process Gas Cooling and Acid Condensation
The process gas will leave the last catalyst bed with a temperature typically between 400 and 450ºC and will typically contain SO_3 plus water vapour. Before the process gas enters the WSA condenser, the temperature must be reduced to a level acceptable to the construction materials of the condenser, which is maximum 290ºC. As will be described below, the process gas cooling forming sulphuric acid in gas phase can be performed in several ways, and contributes substantially to the excellent heat efficiency of the WSA technology. It is, however, equally essential that the process gas temperature is kept well above the sulphuric acid dew point, thus ensuring that no condensation of acid takes place outside the WSA condenser.

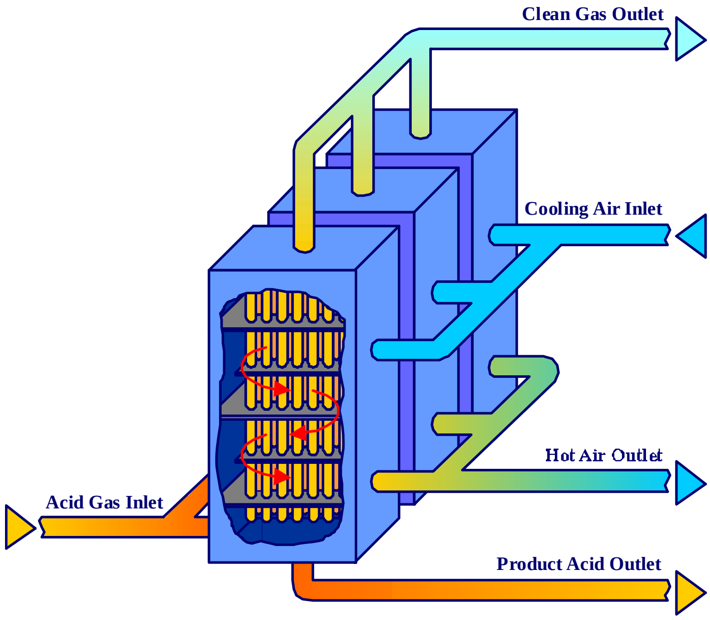

Fig. 2 - Principle design of the WSA Condenser

The patented WSA condenser, as schematically shown in figure 2, is a vertical shell and tube falling film condenser/concentrator with tubes made of acid and shock resistant boron-silicate glass. While the process gas flows upwards inside the tubes, which are cooled on the shell side by ambient air, the sulphuric acid condenses on the tube walls. When flowing downwards and meeting the hot process gas, the acid will be concentrated to typically 98% wt.

The WSA condenser generates hot air at a temperature of 200 - 240ºC, which may be used either for SO_2 gas preheating or as combustion air, as described above, thus recovering heat of sulphuric acid condensation.

The clean process gas leaves the condenser at approximately 100ºC and can usually be sent directly to stack without further treatment, it being a distinct feature of the WSA technology that the clean gas contains only a very low amount of acid mist.

Sulphuric Acid Cooling

The sulphuric acid leaves the condenser at the condensation temperature, typically in the order of 250-260ºC. By recirculation of cold acid, the hot acid is cooled immediately when leaving the acid collector of the condenser to a temperature acceptable to the fluorpolymer lined acid piping and to the plate type acid cooler with plates in Hastelloy. Figure 3 shows a cooling and recirculation system in a WSA plant producing 895 MTPD acid.

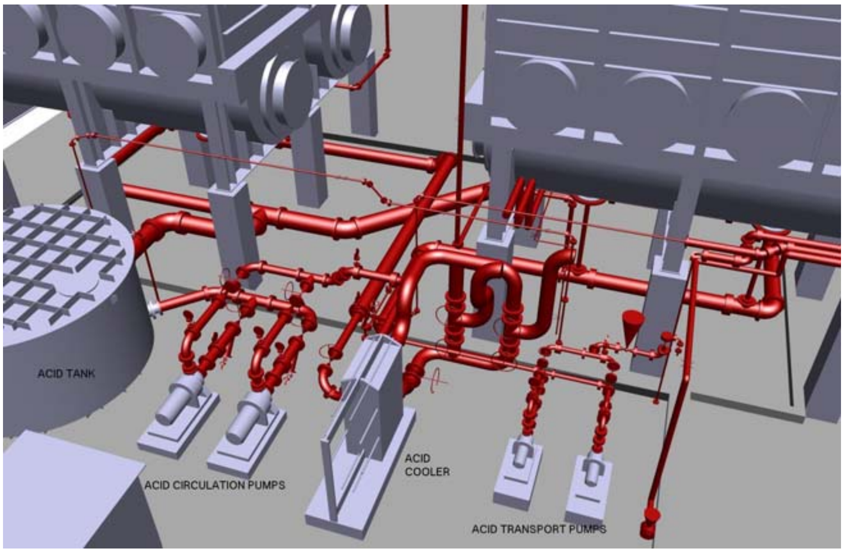

Fig. 3 - Acid cooling and recirculation system for a WSA plant producing 895 MTPD, 98% wt. acid at OAO Kazzinc, Kazakhstan

3. WSA Process Lay-out

Figure 4 shows schematically the process lay-out of a WSA plant of the most recent design for treatment of SO_2 gases in the metallurgical industry.

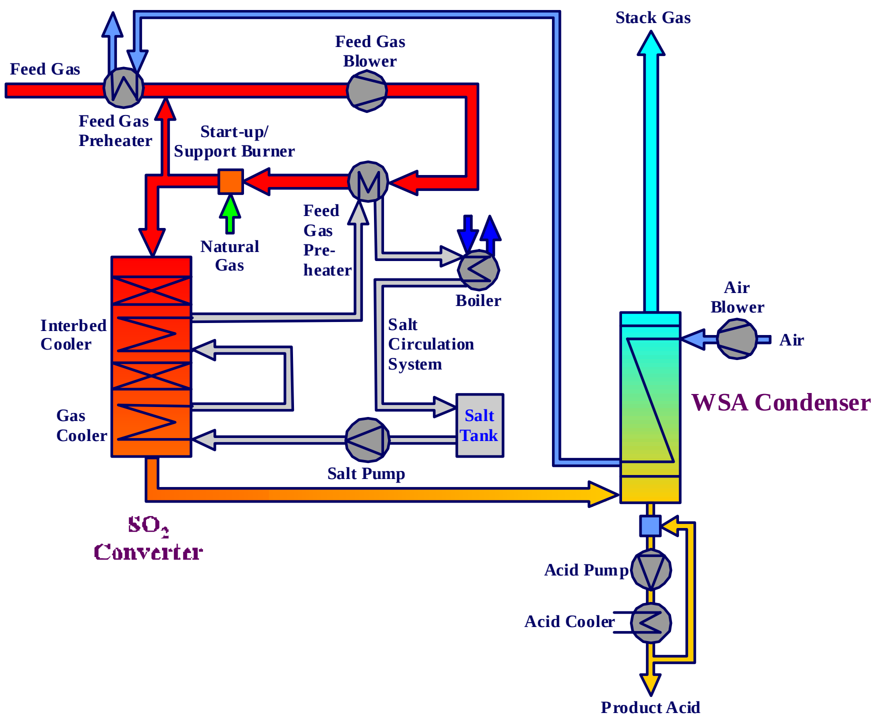

Fig. 4 - State of art process layout of WSA plants in the metallurgical industry

Hot air generated in the WSA condenser is used for the first preheat of the SO_2 feed gas up to a temperature of approximately 150ºC.

Further heat management is performed by means of a system of circulating molten salt. The salt consists of a water free mixture of potassium and sodium nitrate and nitrite, which has a melting point of 150-160ºC. In short, the salt melt circulates between the heat exchangers in the plant. Thus, the melt cools the process gas leaving the first catalyst bed to the optimum temperature at the inlet to the second catalyst bed, and further cools the process gas leaving the second catalyst bed to the temperature of 280-290ºC, before the gas enters the WSA condenser. By circulation of the melt, the recovered heat is displaced to the process feed gas by means of the second feed gas preheater. Surplus heat will be removed in the salt cooler/boiler, and excess energy therefore exported as high pressure steam. The amount of steam export is determined by the SO_2 content in the feed gas.

With this system, it is extremely easy to control the process gas temperatures, and the optimum operating conditions in the SO_2 converter can therefore be sustained at all times.

The heat exchangers in the SO_2 converter, which is shown as a two bed converter, but also could contain three catalyst beds if requirements to SO_2 conversion so dictates, are fully integrated into the converter shell, thereby reducing the amount of ductwork to a minimum.

4. Minimum Consumption of Utilities

Conservation of resources is inherent in the process design of a WSA plant, both with respect to electric power, thermal energy and cooling water.

Electric Power
With the need for drying of the process gas prior to further processing being eliminated and with heat exchangers incorporated in the SO_2 converter shell, it is obvious that the total number of itemized equipment is very low, and the amount of ductwork is therefore also reduced to a minimum. This, together with the low pressure drop over the WSA condenser, as compared to the pressure drop over conventional absorbers, results in a total pressure drop on the process gas side for a plant, as shown in figure 4, as low as approximately 100 mbar, and on the cooling air side, as low as 40 mbar.

This translates into a power consumption of only 45-50 kWh/MT produced acid, when processing a gas received at battery limit at 0 barg with 6% SO_2.

Thermal Energy

The chemical reactions involved in production of sulphuric acid from sulphur dioxide are highly exothermal.

SO_2 oxidation:

$SO_2 + ½O_2 \rightarrow SO_3$ + 99 kJ/mole (242,000 kcal/MT acid)

SO_3 hydration:

$SO_3 + H_2O \rightarrow H_2SO_4$ (gas) + 101 kJ/mole (247,000 kcal/MT acid)

H_2SO_4 condensation:

H_2SO_4 gas $\rightarrow$ H_2SO_4 liquid + 90 kJ/mole (219,000 kcal/MT acid)

Whereas it is state of art in all known sulphuric acid technologies to recover the heat of SO_2 oxidation, only very few technologies are capable of recovering the heat of SO_3 hydration and the heat of sulphuric acid condensation. For instance, in sulphuric acid technologies based on absorption, the heat from these two sources, which is essentially equal to the heat of absorption of SO_3 in the absorbers, is lost to the cooling water.

In the WSA technology, both the heat of SO_3 hydration, and the heat of sulphuric acid condensation are recovered to a very high degree.

As described above, the process gas leaving the last catalyst bed in the SO_2 converter is cooled to a temperature of approximately 290ºC in the final gas cooler, which is integrated in the converter. At this temperature, a large part of the SO_3 will be hydrated to H_2SO_4 on gas form. The corresponding amount of the heat of hydration will therefore be recovered in the molten salt heat displacement system and available for process feed gas preheating in the second process feed gas preheater and/or for production of steam.

The remaining hydration of SO_3 together with condensation of the sulphuric acid will take place in the WSA condenser in which the process gas is cooled to 100ºC. The corresponding amounts of heat will be removed by means of ambient air, resulting in generation of a hot air stream with a temperature of approximately 200-240ºC. This hot air is, as described above, available for process gas preheating in the first process gas preheater.

In consequence, the WSA technology is extremely efficient with respect to thermal energy conservation. This is illustrated by the fact that a WSA plant is capable of operating autothermally, i.e. without use of support fuel for process gas preheating, when processing feed gas with an SO_2 content as low as 3%, whereas other sulphuric acid technologies, not capable of recovering the heat of hydration and condensation, will need an SO_2 concentration of 6-7% in order to operate autothermally.

Cooling Water
Cooling water is used only for cooling of the produced sulphuric acid from the temperature of condensation, typically 250-260ºC, down to the storage temperature of typically 30-40ºC. Therefore the cooling requirement is only 80,000 - 90,000 kcal/MT produced acid, corresponding to a cooling water flow of 8-9 m^3/MT produced acid at a temperature increase of the cooling water of 10ºC.

5. Environmental Considerations

When designing and operating a sulphuric acid plant, environmental considerations essentially concentrate on emissions to the atmosphere of SO_2 and acid mist.

SO_2 Emission
Most national environmental legislations related to SO_2 emissions, including *the American Code of Federal Regulations, Protection of Environment* make distinction between emissions from dedicated sulphuric acid production units, e.g. based on elemental sulphur or roasting of pyrite and other sulphuric acid production units, constructed for the purpose of controlling SO_2 emissions from fatal SO_2 sources. Most SO_2 fixation plants in the metallurgical industry will fall in the second category with less strict requirements to SO_2 removal efficiency than plants falling in the first category.

All newer WSA plants in the metallurgical industry feature two catalyst beds in the SO_2 converter, as shown in figure 4, and a charge of conventional SO_2 oxidation catalyst of the Topsoe VK-series with an inlet operation temperature of approximately 410ºC.

With this design, it is, depending on the SO_2 concentration in the process gas, possible to achieve an SO_2 conversion of between 98-99%, which conversion has proved sufficient in most cases.

However, when the Chilean company Molibdenos y Metales S.A., Santiago at the beginning of 2005 decided to construct a new WSA plant at their molybdenum sulphide roasting facility in Santiago de Chile, the environmental authorities required that the SO_2 conversion was increased as the roasting facility is situated in a densely populated area close to the city of Santiago de Chile. Therefore, the new WSA plant, which is the 4th WSA plant in operation at the Molymet group, is equipped with an SO_2 converter featuring three catalyst beds with conventional catalyst in the two upper beds, and a low temperature, alkali promoted catalyst in the last bed. With this configuration, an SO_2 conversion of 99.6% is achieved.

Acid Mist
The design and operating conditions of the WSA condenser ensure a very low content of acid mist in the clean process gas leaving the WSA condenser, and usually a mist content of less than 10 vol. ppm is achieved. In spite of this, a few clients have decided to install a mist filter at the clean process gas outlet duct, often dictated by local environmental authorities' requirements.

Two main options based on different operating principles (the so-called candle filters and wet electrostatic precipitators respectively) are available for mist filtration.

6. Case Story for Votorantim Metais Zinco, Brazil

After having studied several alternatives for the sulphuric acid plant to be installed at their new lead smelting plant in Juiz de Fora, Votorantim Metais selected the WSA technology. This decision was taken after a detailed study of conventional DC/DA technology, regenerative SO_2 absorption technology (combined with a sulphuric acid plant using the generated SO_2 as feed) and finally the WSA technology. After careful investigation, Votorantim signed a contract with Topsoe for license and engineering and shortly after also a contract for equipment and catalyst.

Most of the equipment and materials will be supplied by Topsoe, however, local supplies will also be made, still under full process responsibility of Topsoe. The plant is scheduled for delivery in 15 months and will then be installed by Votorantim and be ready for operation in the middle of 2009. The WSA plant is equipped with a hydrogen peroxide tail gas scrubber in order to achieve even lower SO_2 emission. Using hydrogen peroxide instead of the cheaper sodium hydroxide as scrubbing medium means that the resulting semi-concentrated sulphuric acid can be directly mixed with the main product sulphuric acid without jeopardising the product acid quality and without creating a secondary disposal problem.

The WSA plant will treat up to 18,000 Nm^3/h with up to 12.6% SO_2 and produce maximum 240 MTPD 98% acid.

During a normal 7.5-hour lead plant process cycle, the WSA plant will receive the process gas in the following three modes:

Smelting 6 h:	Approximately 18,000 Nm^3/h with 12.6% SO_2
Reduction 1 h:	Approximately 21,000 Nm^3/h with 0.23% SO_2
Slag tapping ½ h:	Approximately 7,600 Nm^3/h with 0% SO_2

For the first six hours, the process gas is automatically diluted with fresh air to reach an SO_2 concentration of some 6%. In the reduction and the slag tapping phases, a small amount of liquid SO_2 is added to the process gas to maintain a small amount of SO_2 going to the catalyst beds. The preferred minimum concentration is about 0.1% (vol.) of SO_2.

When the process switches between the three modes, it is important to control the WSA plant's cooling media feed to both the salt heat exchangers as well as the cooling air to the condenser. A feed forward control philosophy, based on measurement of process gas flow, SO_2 concentration and O_2 concentration gives a smooth and trouble-free transition between the operation modes by ensuring exactly the right cooling capacity.

When in operation, the WSA plant will in average produce 200 MTPD of sulphuric acid 98% and export approximately 2.3 t/h of steam, which can be supplied at up to 40 Barg. Additionally, a hot air stream of approx. 50,000 Nm^3/h at 190°C is available from the unit when operating in the smelter mode. This stream can be used for other heating purposes outside the WSA plant.

This will all generate an approximate net income of USD 6 million per year, and at the same time fulfil the local requirement of emitting less than 2 kg of SO_2 per produced ton of sulphuric acid, and less than 0.075 kg of acid mist per produced ton of sulphuric acid.

Consumption	**Specification**	**Annual Cost/ Earning USD**	**Assumption**
Cooling water	80 m^3/h	-17,000	25 USD/1,000 m^3
Power	525 kWh/h	-365,000	83 USD/MWh
Fuel	N.A.	N.A.	N.A.
H_2O_2	28 kg/h	-102,000	50% solution 450 USD/T
SO_2	115 kg/h	-144,500	150 USD/T
Production			
H_2SO_4	8.2 T/h	+6,290,000	90 USD/T
Steam	2.3 T/h	+297,500	15 USD/T
Operating income		+5,959,000	

Table 1 - Annual cost/earning for the Votorantim WSA plant

This calculation is based on an average estimate for a 7.5-hour total operating cycle.

7. Conclusion

The WSA technology has been constantly developed and improved during the past two decades, and the list of references now counts 65 plants in a variety of industries treating sulphurous feed stocks, ranging from concentrated hydrogen sulphide gas, over spent alkylation acid, to both lean and strong SO_2 gas in the metallurgical industry. Out of this number, ten of the WSA plants are installed in the metallurgical industry.

The technology features a very high degree of energy efficiency, meaning that gases containing as little as 3% vol. SO_2 allow autothermal operation. Moreover, the consumption of utilities, such as electric power and in particular cooling water, is extremely low.

The technology is flexible towards variations in SO_2 gas flow as well as SO_2 concentration due to the "built in" feed forward control of the cooling systems.

The only product streams from a WSA plant are commercial quality, concentrated sulphuric acid, clean process gas and steam, and no solid or liquid effluents needing subsequent treatments are produced.

The WSA technology is also an attractive alternative for small to medium-sized plants, producing sulphuric acid from elemental molten sulphur.

Fig. 5 – WSA plant at a Molybdenum Roasting Plant at Molymex, Mexico