

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO	
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TRA: 11 PCT-PATENTE DE INVENCION CAPITULOS I Y II	FOLIOS: 6
ACT: 430 REQUERSOLICITA	

DIRECCIÓN DE NUEVAS CREACIONES

2020
Bogotá, D.C.,

Abogado(a)/Señor(a)
DANILO ROMERO RAAD

Asunto: Radicación: 13-264626- -5
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Patente de Invención	X			Patente de Modelo de Utilidad	
Vía Nacional					
Vía PCT (Fase Nacional)	X	Capítulo I	X	Capítulo II	
No. Solicitud Internacional	PCT/CA2012/000377				
Fecha de Presentación Internacional	20/04/2012				

Como resultado del Examen de Fondo realizado, con fundamento en el Artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se comunica:

1. Documentos estudiados

Descripción:	Rad. N° 13-264626-00000-0000	8/Noviembre/2013
Reivindicaciones:	Rad. N° 13-264626-00004-0000	9/Diciembre/2014
Dibujos:	Rad. N° 13-264626-00000-0000	8/Noviembre/2013
Prioridad:	CA 2737825	20/Abril/2011

2. Análisis de la Prioridad

Se acepta la reivindicación de Prioridad porque esta solicitud fue presentada dentro del plazo establecido (Art. 9 D 486) y su contenido técnico corresponde con el de la prioridad reivindicada.

3. Objeto de la invención

De acuerdo con lo establecido en el numeral 1.2.2.2 del Capítulo Primero del Título X de la Circular Única para efectos del examen de patentabilidad, se tendrá en cuenta la tasa pagada por el solicitante al momento de comenzar el examen para las reivindicaciones adicionales; esto es que cuando la solicitud contenga más de diez (10) reivindicaciones y no se haya pagado la tasa complementaria, sólo se estudiarán las cubiertas por la tasa pagada. Por lo tanto se estudiaran las reivindicaciones 1 a 12.

Título de la solicitud: “Conversión de gas ácido a fertilizantes a base de sulfato o fosfato” (Pág. 3, radicado N° 13-264626-00000-0000).

Expediente 13-264626- -5

El problema planteado en esta solicitud consiste en la necesidad de aprovechar las corrientes de gases ácidos, obtenidas como subproductos de la industria petroquímica, para transformarlas en productos fertilizantes.

Para resolver este problema técnico, la solicitud en estudio proporciona un método para producir un fertilizante a base de sulfato o a base de fosfato a partir de una corriente de un gas como el sulfuro de hidrógeno.

El objeto de la presente Solicitud se relaciona con la Clasificación Internacional de Patentes (CIP): C05F 11/00, C05D 1/00, C01B 17/74, C05D 9/00, C05B 11/08, C10J 3/00, C05C 3/00.

4. Reivindicaciones relativas a un uso (Art 14)

El uso de la reivindicación 12 no es patentable, de acuerdo con el Art 14, ya que en dicha reivindicación se especifica la utilización de una corriente de vapor generada en un generador de vapor para la obtención de electricidad.

5. De la Solicitud de Patente

Reivindicaciones (Art 30 D 486, Art 22 PCT)

La reivindicaciones 1 a 4, 6, 8 y 11 no son claras porque las expresiones *“corriente de desechos o de subproductos”, “gas ácido”, “mineral”, “una sal de potasio”, “agentes de dispersión”, “agentes de aglomeración”, “agentes de recubrimiento”, “agentes para incrementar la resistencia al aplastamiento y la protección contra la humedad”, “agentes de control de polvo” y “agentes que ayudan a la granulación”* son generales y no permiten distinguir la invención del estado de la técnica. Se sugiere sustituirla por un término preciso o un rango concreto.

La reivindicación 12 no es clara porque indica el uso del vapor producido en el generador de vapor para la obtención de electricidad.

Descripción (Art 28 D 486)

La descripción, aunque es clara y permite a la persona versada en la materia comprender el objeto de la solicitud, presenta algunos errores que pueden generar confusión, por lo que se sugiere una revisión de la redacción de la descripción:

Pág. 3, Párr. 4: se encuentra la expresión *“adsorción de solventes”*, la cual no es adecuada al proceso descrito. La expresión correcta es *“adsorción con solventes”*.

Pág. 4, Párr. 2: al sulfuro de hidrógeno se le denomina *“hidrógeno de sulfuro”*, lo cual no es correcto.

A lo largo de la descripción se emplea la expresión *“materia primera”* para designar a las materias primas. Se sugiere corregir dicha expresión.

La expresión *“incorporación”* se emplea a lo largo de la descripción para referirse a la implementación de la invención descrita, lo cual es incorrecto. Se sugiere emplear la expresión *“implementación”*.

Pág. 12, Párr. 4 y Párr. 5: se usa la expresión *“puede ser reactivado”*, la cual no es correcta. Se sugiere emplear la expresión *“puede hacerse reaccionar”*.

6. Determinación del Estado de la Técnica

El estado de la técnica se determinó con base en la fecha de presentación de la solicitud de prioridad invocada, es decir, 20 de Abril de 2011.

Consultadas las fuentes de información con que se cuenta, se encontraron los siguientes documentos que anticipan el objeto de esta solicitud.

Ítem	Documento	Título	Fecha de Publicación
D1	Art 1 ¹	“WSA meeting industry demands”	2007
D2	Libro 1 ²	“Tecnología de los fertilizantes”	1971

El documento D1 divulga método para la transformación de una corriente gaseosa que contiene sulfuro de hidrógeno (Pág. 82, Pág. 80, Fig. 2).

El documento D2 divulga métodos de producción de fertilizantes a base de ácido sulfúrico que reacciona con sales de potasio o fosfatos (Págs 45 y 67).

7. Examen de Patentabilidad (Art 14 D486)

Nivel inventivo (Art 18 D486)

La reivindicación 1 consiste en “*Un método para producir un fertilizante a base de sulfato o de fosfato...*” (Ver Pág. 12 del Rad. N° 13-264626-0004-0000).

Comparación de las características técnicas **esenciales**, con las del Estado de la Técnica:

Características esenciales	D1	D2
Método para producir un fertilizante a base de sulfato o de fosfato a partir de una corriente de desechos o de subproductos que comprende sulfuro de hidrógeno, dicho método comprende:	Transformación del sulfuro de hidrógeno en ácido sulfúrico (Pág. 82, Pág. 80, Fig. 2).	Método de producción de fertilizante a base de roca fosfórica (Pág. 45).
a. Crear una corriente de materia prima a partir de la corriente de desechos o de subproductos;	Se tiene subproductos de la gasificación de carbón o de la industria petroquímica (Pág. 80).	No se menciona
b. Alimentar la corriente de materia prima y aire a un horno;	La corriente de sulfuro de hidrogeno se mezcla con aire y se introduce a una cámara de combustión (Pág. 82, Pág. 80, Fig. 2).	No se menciona
c. Quemar la corriente de gas ácido para producir una corriente que comprenda dióxido de azufre;	El dióxido de azufre es formado en el horno (Pág. 82, Pág. 80, Fig. 2).	No se menciona
d. Alimentar la corriente de dióxido de azufre a un reactor para producir una corriente que comprenda ácido sulfúrico y una corriente de desechos gaseosos; y	El dióxido de azufre formado en el horno se conduce a través de un lecho con catalizador y el trióxido de azufre es absorbido para formar ácido sulfúrico (Pág. 82, Pág. 80, Fig. 2).	No se menciona
e. hacer reaccionar el ácido sulfúrico con potasio o fosfato para convertir el ácido sulfúrico a un fertilizante a base de fosfato o sulfato.	No se menciona	Se tiene la roca fosfórica y se le adiciona ácido sulfúrico para producir ácido fosfórico, superfosfato o fosfato de amonio, se tiene como subproducto sulfato de calcio (Pág. 45).

¹JK Laursen y FE Jensen. Sulphur 312.Haldor Topsoe. Septiembre-octubre 2007

²P. Morel. Editorial Andrés Bello. 1971. Págs. 36, 45 y 67. books.google.es/books?id=OhUHNrsc8MC

Los documentos D1 y D2 se consideran el estado de la técnica más cercano a la invención definida en la reivindicación 1, pues divulgan métodos de obtención de ácido sulfúrico y de fertilizantes.

La diferencia entre la invención, definida en la reivindicación 1, y el método descrito en el documento D1 consiste en que en el documento D1 no se mencionan la posibilidad de generar fertilizantes a partir de ácido sulfúrico.

La diferencia entre la invención, definida en la reivindicación 1, y el método descrito en el documento D2 consiste en que en el documento D2 no se menciona el proceso de obtención del ácido sulfúrico a partir del sulfuro de hidrógeno.

El efecto que logra hacer reaccionar el ácido sulfúrico con una fuente de potasio o fosfato es lograr fertilizantes a base de fosfato o sulfato de manera más eficiente.

Por lo tanto, el problema técnico objetivo que pretende resolver esta invención se puede formular así “¿cómo modificar el método descrito en el documento D1 para obtener fertilizantes a base de fosfato o sulfato de manera más eficiente?”.

Sin embargo, el empleo de ácido sulfúrico para la producción de fertilizantes a base de fosfato ya ha sido reportado por el documento D2, que se refiere a un método para la obtención de ácido fosfórico, fosfato de amonio o superfosfato (Pág. 45).

En consecuencia, una persona normalmente versada en la materia incluiría la reacción del ácido sulfúrico con la roca fosfórica del documento D2 en el método de la anterioridad D1 para llegar así al objeto de la reivindicación 1, lo cual es considerado obvio y, por lo tanto, sin altura inventiva.

Asimismo, el documento D1 divulga las características de las reivindicaciones dependientes, así:

Reivindicación 2: el sulfuro de hidrogeno proviene de un tratamiento con aminos (gas a margo) o proceso de gasificación del carbón (Pág. 80).

Reivindicación 11: en el proceso WSA se evita la deshumidificación del proceso tradicional pero igualmente se recupera calor en el enfriamiento del dióxido de azufre para la generación de vapor (Pág. 82, Pág. 80, Fig. 1).

Adicionalmente, el documento D2 divulga las características de las reivindicaciones dependientes, así:

Reivindicación 3: se tiene como fuente de fosfato una roca o mineral que contiene fosfato (Pág. 45).

Reivindicación 4: como fuente de potasio se tiene cloruro de potasio (Pág. 67).

Reivindicación 7: Se tiene la roca fosfórica y se le adiciona ácido sulfúrico para producir ácido fosfórico, superfosfato o fosfato de amonio, se tiene como subproducto sulfato de calcio (Pág. 45).

Reivindicación 8: se tiene como fuente de fosfato una roca o mineral que contiene fosfato (Pág. 45).

Reivindicación 10: se hace reaccionar ácido sulfúrico con cloruro de potasio para obtener sulfato de potasio y como subproducto ácido clorhídrico, en donde dependiendo de la relación estequiometría y el reactivo limitante se puede tener ácido sulfúrico como producto que no reaccionó, el cual es un ácido débil en su segunda disociación (Pág. 67).

Por otra parte las reivindicaciones 5, 6, 9 y 12 se afectan con el conocimiento del técnico, *“el experto medio deberá poseer experiencia y contar con un saber general en la materia y con una serie de conocimientos en el campo específico de la invención”*³, el cual conoce que:

Reivindicación 5: se adiciona magnesio como micronutriente al fertilizante⁴ (Pág. 4, diagrama de flujo).

Reivindicación 6: Para mantener las propiedades de los fertilizantes se les da una forma granulada y se les espolvorea con determinados aditivos⁵ (Pág. 243).

Reivindicación 9: se tiene la acidificación del óxido de zinc con ácido sulfúrico para producir sulfato ⁶ (Pág. 7, Párr. 3).

Reivindicación 12: la corriente de salida del generador de vapor es utilizada para producir electricidad⁷ (Pág. 2).

8. Conclusión

Los requisitos de Patentabilidad de la presente Solicitud están afectados así:

Ítem	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	Art 1	1 a 12	Nivel inventivo
D2	Libro 1	1 a 12	Nivel inventivo

9. Respuesta a los argumentos del señor solicitante

Argumentos con respecto al estudio de novedad y nivel inventivo

La solicitante indica que el nuevo capítulo reivindicatorio modificado con respecto al estudiado en el Oficio 9290 presenta novedad/nivel inventivo con relación al documento US2067311 (D1) y nivel inventivo con respecto a los documentos WO2008022461A1 (D2) y US 2003442 (D3), ya que el fertilizante a base de fosfato o sulfato no se encuentra mencionado en D1.

Con respecto a lo anterior, se aclara que se realiza un nuevo estudio de patentabilidad en donde se encuentra que con los nuevos documentos D1 y D2 se afecta el nuevo capítulo reivindicatorio por nivel inventivo.

Por otro lado la solicitante afirma que al mencionar unas cuantas reacciones químicas por separado a los documentos D1 y D2 como conocidas en el estado de la técnica no se observa la invención como un todo, esta Oficina encuentra que dichas reacciones que producen fertilizantes, como por ejemplo la de obtención de sulfato de potasio y ácido clorhídrico a partir de ácido sulfúrico y cloruro de potasio, son conocimiento del técnico versado en la materia que indican claramente cómo se puede emplear el ácido sulfúrico para la obtención de un fertilizante específico.

³Proceso 43-IP-2002, publicado en la G.O.A.C. N° 870, de 9 de diciembre de 2002, caso: formulaciones de péptidos hidrosolubles de liberación retardada.

⁴ Best Available Techniques for Pollution Prevention and Control in the European Sulphuric Acid and Fertilizer Industries. Booklet No. 3 of 8: PRODUCTION OF SULPHURIC ACID. Fertilizers Europa. 2000 Edition. Pág. 4, diagrama de flujo.

⁵A. Finck. Fertilizantes y fertilización. Editorial Reverté S.A. 1988. Pág. 243. books.google.es/books?isbn=8429110100.

⁶RG Menom. The basic of zinc in crop production. International fertilizer development center. 1996. Pág. 7, Párr. 3.

⁷K. Quach y G. Robb. Steam Turbine Cogeneration. 2008. Pág.2.

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta (60) días contados a partir del día siguiente de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Se invita al solicitante se sirva indicar, si así lo considera, su renuncia al término faltante de sesenta (60) días para dar respuesta a este requerimiento y presentarla por escrito.

Finalmente, se le recuerda al solicitante que si como respuesta a este requerimiento llegara a modificar el capítulo reivindicatorio y éste contenga más de diez (10) reivindicaciones, no pagará la tasa de modificación voluntaria pero sí la correspondiente al pago por reivindicación adicional.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única No. 10 de 2001.



JOSÉ LUIS SALAZAR LÓPEZ
Director de Nuevas Creaciones (c)

El anterior requerimiento fue notificado por fijación en lista, de fecha 2015-04-21

Elaboró: Jorge Eduardo Cortazar Gomez
Revisó: Olga Ximena Benavides Salazar

PABLO MOREL

Tecnología de los fertilizantes



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car ácido sulfúrico.

Se utilizan dos tipos generales de ácido sulfúrico en la producción de superfosfato y de ácido fosfórico por vía húmeda:

- Acido nuevo o virgen, producido a partir de azufre elemental, piritas, yesos y gases industriales.
- Acido sobrante o de desecho, derivado de industrias que utilizan grandes volúmenes de ácido sulfúrico en el procesamiento de diversos productos. En ciertos casos, este ácido debe ser acondicionado para eliminar sustancias objetables en los fertilizantes.

La conversión de la roca fosfatada en un fertilizante fosfatado soluble tratándola con este ácido es el método preferido de producción. Es de menor costo que el método del horno eléctrico, y los productos se integran mejor al mercado que si se utiliza ácido nítrico. Para convertir la roca fosfatada a ácido fosfórico, se requiere casi una tonelada de azufre por cada tonelada de anhídrido fosfórico producido. Para producir

salmuera de cloruro de potasio para obtener sulfato de potasio.

Proceso Hargreaves: se obtienen directamente sulfato de potasio y ácido clorhídrico a partir de azufre y cloruro de potasio.

Proceso Mannheim: el cloruro de potasio reacciona con el ácido sulfúrico para dar sulfato de potasio y ácido clorhídrico.

—*Sulfato doble de potasio y magnesio*: se fabrica por refinación del mineral langbeinita. Este se mezcla con cloruros de potasio y de sodio. La langbeinita es menos soluble, lo cual constituye la base para la purificación, en la cual el mineral se muele y un proceso de lavado separa las sales cloradas.

—*Nitrato de potasio*: el de grado fertilizante se produce en Vicksburg, Mississippi, haciendo reaccionar ácido nítrico con cloruro de potasio. Hay otros métodos, pero hasta ahora antieconómicos.

5.3.3 *Procesos secundarios*

La creciente demanda por productos fertilizantes granulados ha resultado en el desarrollo y aplicación de técnicas para transformar los materiales finos en productos de partículas mayores. Los dos métodos para convertir el cloruro de potasio fino en partículas aglomeradas mayores son: fusión y compactación. Este segundo es el más nuevo y el de mayor empleo.

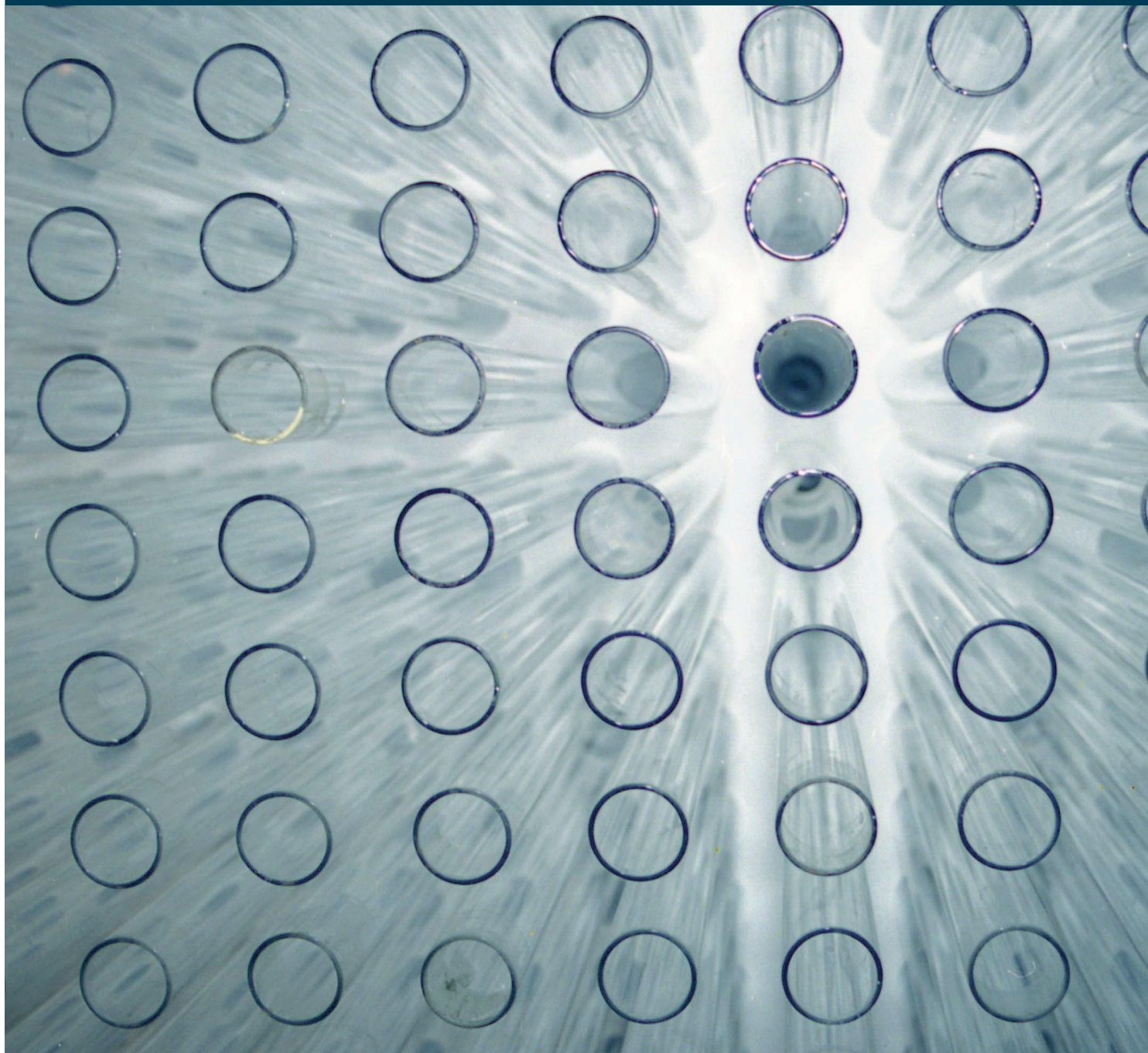
Proceso de fusión: el cloruro de potasio finamente dividido recuperado de la flotación se calienta a una temperatura de 755°C para obtener un fundido que se solidifica por enfriamiento: las escamas así formadas se muelen y se tamizan para obtener el tamaño de partícula deseado.

Este ácido es el punto de partida para varios fertilizantes fosfatados. La roca fosfatada, después de su extracción, transporte a la planta de refinación, refinada y concentrada, se trata con ácido sulfúrico en mayor proporción que para producir superfosfato normal. Después de una filtración, se obtiene un ácido fosfórico crudo que contiene 28 a 30 por ciento de anhídrido fosfórico. Este ácido puede concentrarse a 40 por ciento para producir fosfato de amonio; a 54 por ciento que es el de transporte comercial o a 72 por ciento que constituye el llamado ácido superfosfórico (ver Esquema 2). La mayor parte de los procesos por vía húmeda dan como subproducto el sulfato de calcio o yeso, que por lo general se desecha. Es acumulado en grandes pilas al aire libre o, si la ubicación lo permite, se lanza al mar. Con la actual escasez de azufre, se están estudiando métodos para recuperarlo de este subproducto. Hay varios procesos eficientes para la producción de ácido fosfórico por vía húmeda, variando el tamaño de las plantas entre 500 a 600 toneladas diarias de anhídrido fosfórico. La producción

WSA

- Meeting industry demands by Jens K. Laursen and Frands E. Jensen

RESEARCH | TECHNOLOGY | CATALYSTS



Meeting industry demands

Jens K. Laursen and **Frands E. Jensen** of Haldor Topsøe A/S give an overview of the process principles of the WSA process for sulphur recovery, providing industry examples from a variety of applications.

The WSA process is a process for the conversion of sulphurous streams into sulphuric acid developed by Haldor Topsøe A/S, Denmark. Since its introduction in the 1980s, the WSA process has been recognised as an efficient process for recovering sulphur from various sources in the form of commercial quality sulphuric acid. The WSA process has found widespread application in the refineries, oil and coal based industries, the metallurgical industry, the steel industry (coking), the power industry, and the cellulose industry. More than 60 plants have now been licensed worldwide for treatment of process gases in a wide range of process industries.

Application

The WSA process is applied in all industries where removal of sulphur is an issue. Typical applications include:

Refinery and petrochemicals

- H₂S-containing gases from amine units
- Sour water stripper gases
- Regeneration of spent sulphuric acid from alkylation
- Treatment of stack gases from boilers fired by heavy residues and petroleum coke

Metallurgical industry

- Off-gases from metal sulphide roasters (Mo, Zn, Pb, Cu, and other)

Coal based industry

- H₂S, NH₃ and HCN containing gases in coking plants
- H₂S, NH₃ and HCN containing gases from coal gasification

- H₂S containing gases in crude benzene processing units

Cellulose industry

- H₂S and CS₂ containing gases in viscose fibre plants

Power industry

- Flue gases from combustion of high-sulphur fuels. Both sulphur oxides and NO_x are removed.

Salient features

Compared to other sulphur treatment processes, the WSA process offers a wider range of features:

- More than 99% recovery of the total sul-

phur content, always in compliance with environmental legislation

- Product is clean, concentrated sulphuric acid of commercial quality, also in turn-down situations
- Heat of reaction is recovered as superheated or saturated steam
- Gases containing hydrocarbons – also very high CO₂ content – are accepted
- Optional DeNO_x for gases with high content of NH₃ and HCN
- No consumption of chemicals (except for optional DeNO_x)
- Very low consumption of cooling water
- No consumption of process water
- No liquid or solid waste effluents
- Wide turndown range
- Simple layout, simple operation, overall attractive economy

Fig 1: WSA process for H₂S gas

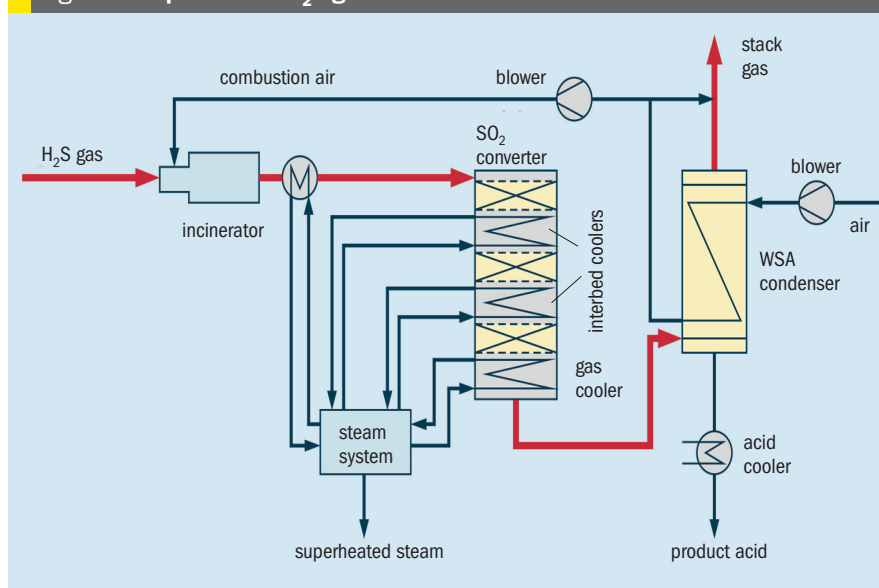
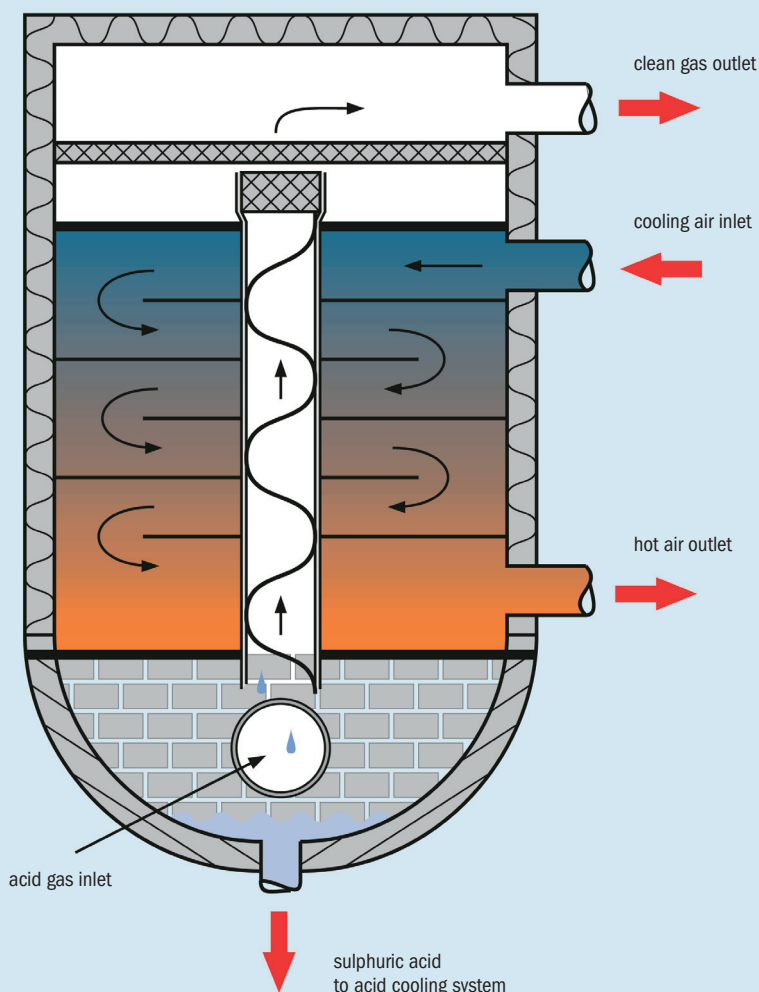


Fig 2: WSA Condenser



Process principles

WSA is short for Wet gas Sulphuric Acid, meaning that contrary to conventional sulphuric acid processes, the WSA process treats the process gas with all of its water content. This means that cooling and condensation prior to the SO_2 conversion stage are not required. Consequently, there will be no liquid waste effluent, no loss of acid, no use of cooling water for this part, and no loss of heat. This feature also reduces pressure drop and thereby electric power consumption.

The process principles can be illustrated by three different cases: One case treating hydrogen sulphide (Fig. 1), one case treating sulphur dioxide (Fig. 3) and one case treating flue gas from combustion of high-sulphur residual oil (Fig. 4). Basically, the same process steps apply for all feed gases:

- Combustion (except in the case of SO_2 gases)
- Heating or cooling of the gas to the reactor temperature
- Conversion of SO_2 to SO_3
- Hydration of the SO_3 to gaseous H_2SO_4
- Condensation of H_2SO_4 in the WSA condenser

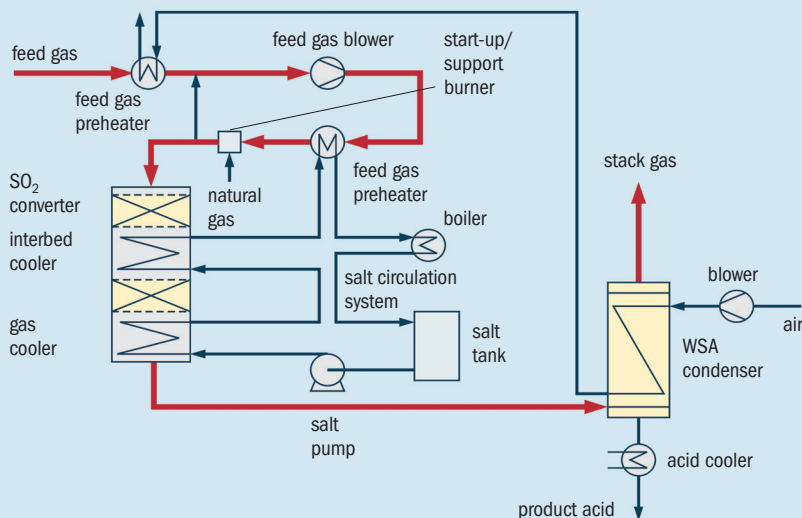
Case 1 – H_2S gases (Fig. 1)

The WSA process is an effective and in some cases superior alternative to the Claus process. The process can be applied for gases with high H_2S content as in amine regenerator off-gas, and for gases with a lower H_2S content as in off-gas from Rectisol units in coal gasification. The latter type of gas typically has a high content of CO_2 and often a substantial content of hydrocarbons; this is also accepted by the WSA process.

In the case of H_2S , e.g. from an amine regeneration unit, the gas is incinerated to SO_2 in a burner followed by a waste heat boiler. Unless the feed gas contains other combustibles, support fuel is necessary if the feed gas contains less than, say, 25% H_2S . The incinerated gas typically contains 5-6% SO_2 and all the water from the combustion of the H_2S and other combustibles. The gas leaving the waste heat boiler has a temperature of approximately 400°C .

The gas then enters the SO_2 reactor which contains two or three catalytic beds, depending on the actual process conditions and the desired degree of conversion. As the reaction in the reactor is exothermal, the gas is cooled between the beds in order

Fig 3: SNOX™ process



to optimise the SO_2/SO_3 equilibrium. After the last conversion stage, the gas is cooled and most of the SO_3 reacts with the water vapour and forms gas phase sulphuric acid (Table 1). The process gas then goes to the WSA condenser where final hydration and condensation of acid takes place.

The WSA condenser (Fig. 2) is a vertical shell-and-tube type falling film condenser and concentrator with tubes made of boron silicate glass resistant to thermal shock and acid. The process gas flows inside the tubes, which are cooled on the outside by ambient air in cross-current flow pattern. Sulphuric acid condenses in the tubes and flows downwards while being concentrated in counter-current contact with the hot process gas. The sulphuric acid is collected in the acid resistant brick-lined bottom part and is cooled to 30-40°C in a water-cooled plate type heat exchanger and then pumped to storage.

The cleaned process gas leaves the WSA condenser at approximately 100°C and can be sent directly to the stack. It is a notable feature of the WSA condenser that the gas contains only a very small amount of acid mist, typically less than statutory requirements.

The cooling air leaves the WSA condenser at approximately 200-250°C. Part of the hot air is used as combustion air in the H_2S burner, and the remaining part can be mixed into the stack for increased buoyancy or it can be used for boiler feed water preheating.

When the feed gas contains appreciable amounts of ammonia, hydrogen cyan-

Table 1: Reactions in WSA and SNOX™ plants

Combustion	$\text{H}_2\text{S} + \frac{3}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{SO}_2$	+ 518 kJ/mole
Oxidation	$\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3$	+ 99 kJ/mole
Hydration	$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \text{ (gas)}$	+ 101 kJ/mole
Condensation	$\text{H}_2\text{SO}_4 \text{ (gas)} + 0.17 \text{ H}_2\text{O (gas)} \rightarrow \text{H}_2\text{SO}_4 \text{ (liq)}$	+ 69 kJ/mole
DeNOx	$\text{NO} + \text{NH}_3 + \frac{1}{4} \text{O}_2 \rightarrow \text{N}_2 + \frac{3}{2} \text{H}_2\text{O}$	+ 410 kJ/mole

ide or other nitrogen compounds, or if the incineration takes place at elevated temperatures, a certain amount of nitrogen oxides (NOx) will be formed. In order to comply with statutory requirements and to avoid discolouration of the stack emission, it may be necessary to remove the NOx. This can conveniently take place in an SCR process stage (Selective Catalytic Reduction) upstream the SO_2 reactor. Ammonia in stoichiometric amounts relative to the NOx content is injected into the process gas which passes over an SCR catalyst whereby the NOx is reduced to nitrogen and water vapour (Table 1).

The heat of reaction is recovered in the form of steam. Saturated steam at typically 50-60 barg is generated in the waste heat boiler and in the gas cooler downstream the SO_2 reactor. Saturated steam drawn from the steam drum is then used for cooling between the catalytic reactor stages and is exported as superheated steam, typically at more than 400°C, or it can be conditioned to the desired properties. The required steam pressure is determined by the content of SO_3 and water in the process gas in such a way that all surface temper-

atures are well above the acid dew point.

The construction materials of the WSA plant is generally carbon steel, except where design temperature necessitates heat resistant steel (stainless or $\frac{1}{2}$ Mo alloy). The combustion chamber of the H_2S burner and the waste heat boiler inlet are protected by refractory lining. The parts of the WSA condenser in contact with condensing acid will be protected by a fluoro-polymer lining, and the bottom of the condenser is lined with acid resistant bricks. The acid cooler is typically made of Hastelloy C. The acid pump is lined and has magnetic coupling.

For example, in a large refinery expansion project, TNK-BP in Ryazan, Russia decided to use WSA for the sulphur recovery of the entire site, including SWS gas treatment. This decision was made based on eight years of successful operation of two other WSA plants on the site. Alkylation was part of the expansion and naturally it was decided to incorporate acid regeneration in the overall system; in this case the H_2S capacity was much more than needed as fuel for the spent acid regeneration. Two separate WSA plants were built, one for H_2S plus SWS gas, including SCR reactor,

Fig 4: WSA process for SO_2 gas

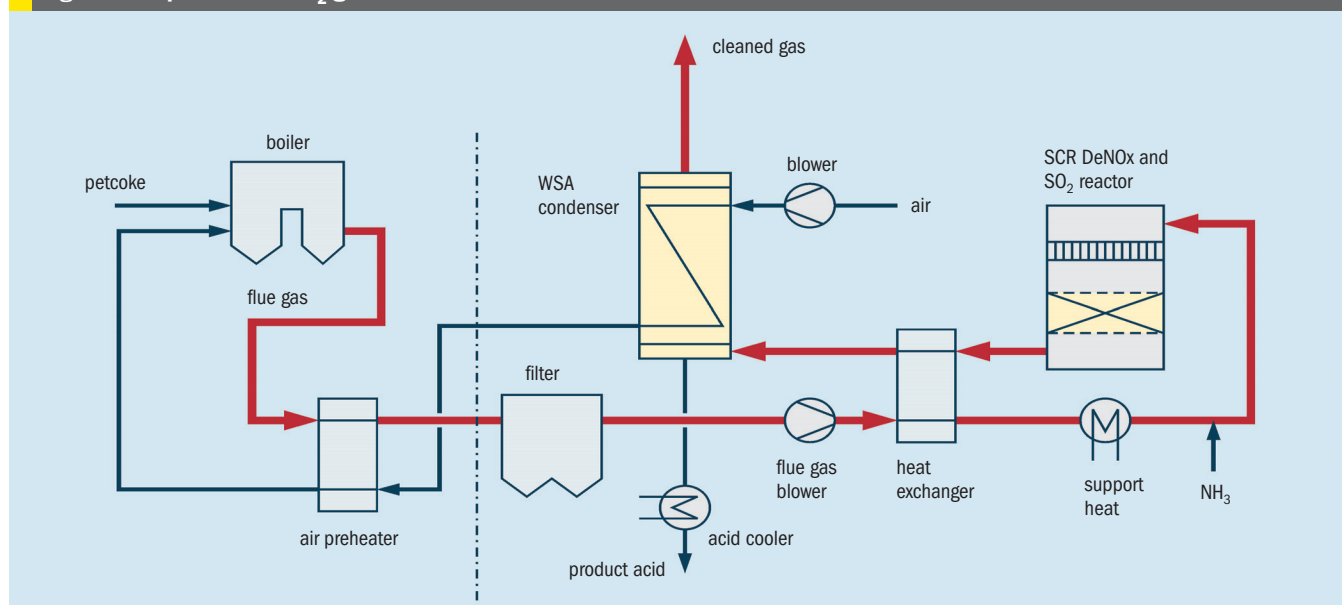


Table 2: Key parameters of WSA plants for H₂S gas

	Plant A	Plant B
Spent acid		
H ₂ O, wt-%	4	-
H ₂ SO ₄ , wt-%	90	-
Hydrocarbons, wt-%	6	-
Acid gas		
H ₂ S, vol-%	91	91
SWS gas		
NH ₃ , vol-%	-	53
H ₂ S, vol-%	-	47
Typical performance		
Spent acid, t/d	100	-
Acid production, t/d	330	400
Acid concentration, wt-%	98	98
Steam production, t/h	25	45
Cooling water consumption, m ³ /h	125	195

Table 3: Key Parameters of WSA Plant for SO₂ Gas

Flow of feed gas, Nm ³ /h	60,000
SO ₂ concentration, vol-%	1.40–3.75
Typical performance	
Acid production, t/d	170
Acid concentration, wt-%	98
Cooling water consumption, m ³ /h	57

Table 4: Key parameters of SNOX™ plants

	Raffineria di Gela, Italy	OMV, Austria
Fuel	Petcoke, residue	residue
Sulphur in fuel, wt-%	5-7	4
Flue gas vol., Nm ³ /h	1,200,000	820,000
SO ₂ in flue gas, mg/Nm ³	10,000	7,000
Typical performance		
Acid production, t/d	440	220
Acid concentration, wt-%	94-95	94-95

and one for spent acid plus H₂S. The new WSA plants were started up in 2005 and 2006, respectively. Table 2 shows the key parameters of the two plants.

Case 2 – SO₂ gases (Fig. 3)

In the case of SO₂ gases, e.g. from a minerals roaster, the feed gas is received from a scrubbing unit upstream of the WSA plant at a temperature of around 40°C, saturated with water, free from particulates, and typically containing some SO₃. In order to avoid corrosion of downstream equipment, the temperature is increased by heating with hot air from the WSA condenser in a glass-tube gas/gas heat exchanger. In most

cases a heat distribution system with molten salt is applied to recover the heat of reaction and deliver it to preheat the SO₂ gas to the operating temperature of the SO₂ converter. If the content of SO₂ is in the order of 3 vol-% or higher, there will be sufficient heat in the system to preheat the SO₂ gas. Otherwise support fuel must be applied. Excess heat is exported as steam.

The WSA process is of particular interest for low and medium SO₂ concentrations (1 – 8 vol-%, but depending on the actual application), such as off-gases from smelters of molybdenum, zinc and lead sulphide, and several types of off-gases from copper sulphide smelters. SO₂ gases with higher SO₂

content have to be diluted with air before they can be treated in the WSA process.

For example, the Chilean-based molybdenum group, Molymet, has been operating WSA plants at their molybdenum roasters in Belgium, Chile and Mexico since 1990, 1993 and 2001, respectively. It was therefore natural for Molymet to choose a WSA plant for their expansion project in Nos near Santiago, Chile. This means that they will now have two WSA plants at this site, where the requirements for efficient gas cleaning are high because of the location near Santiago. The new plant was started up successfully in the summer of 2007. Table 3 shows the key parameters of the plant.

Case 3 – Flue gases from combustion of high-sulphur fuels (Fig. 4)

The WSA process principles are also applied for large process gas volumes as in power plants, and units are in operation for both coal fired power plants and for utility boilers (typical unit size is 1 million Nm³/h). Usually, DeNOx is incorporated in such installations. This version of the process is termed SNOX™. The SNOX™ process is more advantageous for fuels with very high sulphur content, and its main application is therefore for combustion of high sulphur residues in refineries rather than for the average coal fired power plant.

When a utility boiler is equipped with a SNOX™ plant, it will be possible to fuel the boiler with very high sulphur residues, petroleum coke, H₂S gas, Claus tail gas, SWS gas and the like. This will bring the SO₂ content of the flue gas to 0.4-0.5% or higher, which is unacceptable to most other FGD processes. Additionally, the SNOX™ process readily accepts SO₃ which is troublesome to other FGD processes. The heat content of the flue gas and the heat of reaction are utilised and returned to the boiler, and substantial revenue is received from sale of the product acid. There are no secondary waste materials, and the only reagent used is ammonia for the DeNOx.

The SNOX™ process is illustrated in Fig. 4. Flue gas from the boiler is cleaned in an electrostatic precipitator and heated by the gas leaving the SO₂ converter in a regenerative or recuperative heat exchanger. After heat exchange, NOx is reduced in the SCR reactor, and the gas is then sent to the SO₂ converter. The converted gas is cooled in the feed/effluent heat exchanger, and further cooling and condensation

takes place in the WSA condenser. The cleaned gas is sent directly to the stack, and the heated cooling air is returned to the boiler, thereby increasing its efficiency.

For example, two large SNOX™ plants are installed at two European oil refineries.

Raffineria di Gela, Italy, is based on heavy crude oil with high sulphur content and coking processes. As environmental regulations have become stricter, proper disposal of the heavy residues and the petroleum coke is a prerequisite for the operation. The refinery boilers are fuelled mostly with petroleum coke, and the SNOX™ process was selected as the only viable process able to deal with the high sulphur flue gases. The SNOX™ plant was started up in 1999.

The Schwechat refinery of OMV, Austria, had an existing flue gas treatment plant installed on its boilers fuelled with heavy residual oil. The existing flue gas treatment plant could not fulfil new environmental requirements, and operation costs could be improved very much by installation of a SNOX™ plant. Therefore, in 2005, it was decided to replace the existing flue gas treatment unit with a SNOX™ plant which

was able to fulfil all statutory requirements in the foreseeable future. The SNOX™ plant will also treat tail gases from the Claus units of the refinery. Start-up is scheduled for October 2007.

Table 4 shows the key parameters of the two plants.

Catalysts

The SO₂ conversion catalysts applied in the WSA and SNOX™ processes are the Topsoe VK-series catalysts. The catalysts are based on vanadium pentoxide and sodium and potassium pyrosulphates on a diatomaceous earth silica carrier material and specially adapted for moist gases. The Topsoe VK-series of catalysts will cover all relevant process conditions and make it possible to select the best catalyst or combination of catalysts for a given performance specification. They are also widely used in conventional dry sulphuric acid plants.

The SCR DeNOx catalyst is one of the Topsoe DNX series catalysts, a corrugated monolithic catalyst based on titanium, tungsten and vanadium as active materials.

Conclusion

The WSA and SNOX™ processes are simple and efficient sulphur recovery processes which meet the demands of the industry for environmental compliance, low energy usage, and low overall operating costs.

Sulphur in any form is recovered as concentrated sulphuric acid of commercial quality. The WSA technology can be applied for a variety of process streams, ranging from flue gases to concentrated H₂S gases as well as for elemental sulphur and various sulphur containing liquid waste materials.

In oil refining, the WSA process is applied for HDS acid gases, spent alkylation acid, Claus tail gases, flue gases, and various combinations hereof. In the metallurgical and other process industries, the WSA process is recognised as a suitable process, in particular for treating of low to medium SO₂ gases. In all cases, the main criteria for selecting the WSA process are low operating costs, the value of the sulphuric acid product, and the absence of secondary effluents. ■



Best Available Techniques for Pollution Prevention and Control in the European Sulphuric Acid and Fertilizer Industries

**Booklet No. 3 of 8:
PRODUCTION OF SULPHURIC ACID**

2000 Edition



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for Pollution Prevention and Control in the
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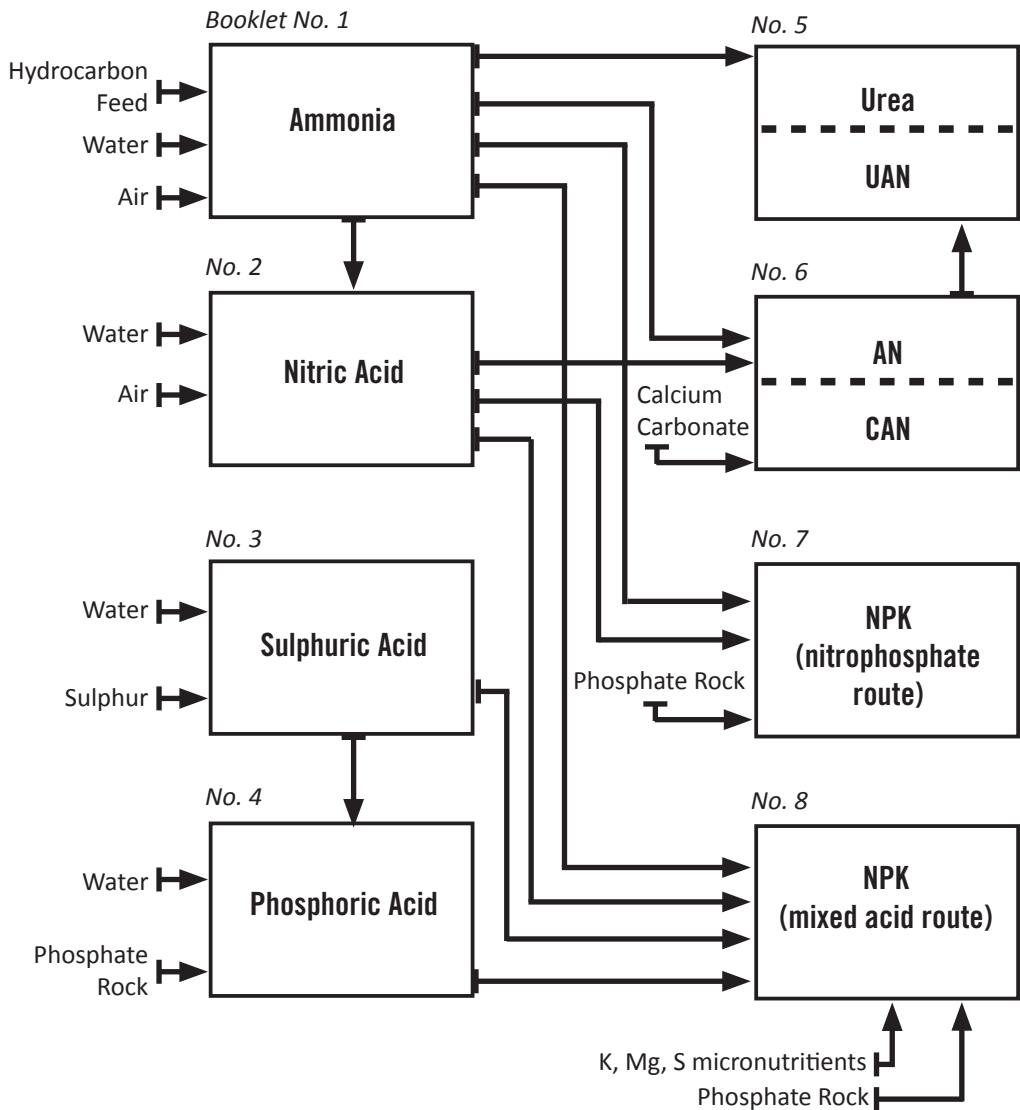
Booklet No. 3 of 8:

**PRODUCTION OF SULPHURIC
ACID**

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Fertilizers Europe BAT Booklets



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PREFACE

The European Sulphuric Acid Association (ESA) and Fertilizers Europe have prepared recommendations on Best Available Techniques (BAT) in response to the EU Directive on integrated pollution prevention and control (IPPC Directive). This Booklet (based on Report EUR 13006 EN) has been prepared by ESA and Fertilizers Europe experts drawn from member companies. The recommendations cover the production processes of Sulphuric Acid and Oleum and reflect the industry perception of which techniques are generally considered to be feasible and present achievable emission levels associated with the manufacturing of the products.

The Booklet uses the same definition of BAT as that given in the IPPC Directive. BAT covers both the technology used and the management practices necessary to operate a plant efficiently and safely. The focus is primarily on the technological processes, since good management is considered to be independent of the process route. The industry recognises, however, that good operational practices are vital for effective environmental management and that the principles of Responsible Care should be adhered to by all companies.

Two sets of BAT emission levels are given:-

- For existing production units where pollution prevention is usually obtained by revamps or end-of-pipe solutions
- For new plants where pollution prevention is integrated in the process design

The emission levels refer to emissions during normal operations of typical sized plants. Other levels may be more appropriate for smaller or larger units and high emissions may occur in start-up and shut-down operations and in emergencies. Only the more significant types of emissions are covered and the emission levels given do not include fugitive emissions and emissions due to rainwater. The emission levels are given both in concentration values (ppm or mg.m^{-3}) and in load values (emission per tonne 100% wt sulphuric acid). It should be noted that there is not necessarily a direct link between the concentration values and the load values.

It is recommended that the given emission levels should be used as reference levels for the establishment of regulatory authorisations. Deviations should be allowed as governed by:-

- **Local environmental requirements**, given that the global and inter-regional environments are not adversely affected
- **Practicalities and costs of achieving BAT**
- **Production constraints** given by product range, energy source and the availability of raw materials

If authorisation is given to exceed these BAT emission levels, the reasons for the deviation should be documented locally. Existing plants should be given ample time to comply with BAT emission levels and care should be taken to reflect the technological differences between new and existing plants when issuing regulatory authorisations, as discussed in this Booklet.

There is a wide variety of methods for monitoring emissions. The emission levels given are subject to some variance, depending on the method chosen and the precision of the analysis. It is important when issuing regulatory authorisations, to identify the monitoring method(s) to be applied. Differences in national practice may give rise to differing results, as the methods are not internationally standardised. The given emission levels should not, therefore, be considered as absolute but as references which are independent of the methods used.

ESA would also advocate a further development for the authorisation of sulphuric acid plants. The plants can be complex, with the integration of several production processes and they can be located close to other industries. Thus there should be a shift away from authorisation governed by concentration values of single point emission sources. It would be better to define maximum allowable load values from an entire operation, e.g. from a total site area. However, this implies that emissions from single units should be allowed to exceed the values in the BAT recommendation, provided that the total load from the whole complex is comparable with that which can be deduced from there. This approach will enable plant management to find the most effective environmental solutions and would be to the benefit of our common environment.

Finally, it should be emphasised that each individual member company of ESA is responsible for deciding how to apply the guiding principles of the BAT Booklet on the Production of Sulphuric Acid.

1. GENERAL INFORMATION

1.1 General Information About the Production of Sulphuric Acid

More sulphuric acid is produced than any other chemical in the world. In Western Europe in 1997 over 19 million tonnes were produced, the total production world-wide being estimated at around 150 million tonnes. About half of this output is produced in North America, Western Europe and Japan [20], [21].

Table 1 World Production and Consumption

In Million tonnes H_2SO_4	1992	1993	1994	1995	1996	1997
World sulphuric acid production	145.7	132.5	137.9	148.9	151.3	155.6
World sulphuric acid consumption	147.1	132.8	138.8	150.1	153.3	157.5

The output of sulphuric acid at base metal smelters today represents about 20% of all acid production. Whereas in 1991 smelter acid production amounted to 27.98 millions tonnes, it is calculated that the output in the following decade will have grown to reach 44.97 millions tonnes in 2001. Smelter acid will be more than 25% of world sulphuric acid production compared to some 18% in 1991.

Table 2 Production of Sulphuric Acid in the Countries of the European Community

In Million tonnes H_2SO_4	1992	1993	1994	1995	1996	1997
Belgium/Luxembourg	1.836	1.535	1.515	2.174	2.067	2.160
Finland	1.351	1.361	1.373	1.376	1.479	1.570
France	3.132	2.515	2.227	2.382	2.263	2.242
Germany	3.800	3.515	3.380	3.530	3.978	3.496
Greece	0.620	0.588	0.630	0.515	0.615	0.675
Italy	1.725	1.423	1.228	1.344	1.588	1.590
Netherlands	1.080	1.000	1.073	1.113	1.060	1.040
Norway	0.587	0.564	0.585	0.609	0.594	0.666
Spain	2.420	2.176	2.348	2.265	2.786	2.810
Sweden	0.567	0.497	0.518	0.485	0.620	0.630
United Kingdom	1.568	1.269	1.225	1.293	1.196	1.205

Sulphuric acid is produced in all the countries of Europe with the major producers being Germany, Spain, France, Belgium and Italy. These countries accounting for 70% of the total European production. It is used directly or indirectly in nearly all industries and is a vital commodity in any national economy. In fact, sulphuric acid is so widely used that its consumption rate, like steel production or electric power, can be used to indicate a nation's prosperity.

Most of its uses are actually indirect in that the sulphuric acid is used as a reagent rather than an ingredient. The largest single sulphuric acid consumer by far is the fertiliser industry. Sulphuric acid is used with phosphate rock in the manufacture of phosphate fertilisers. Smaller amounts are used in the production of ammonium and potassium sulphate. Substantial quantities are used as an acidic dehydrating agent in organic chemical and petrochemical processes, as well as in oil refining. In the metal processing industry, sulphuric acid is used for pickling and descaling steel; for the extraction of copper, uranium and vanadium from ores; and in non-ferrous metal purification and plating. In the inorganic chemical industry, it is used most notably in the production of titanium dioxide.

Certain wood pulping processes for paper also require sulphuric acid, as do some textile and fibres processes (such as rayon and cellulose manufacture) and leather tanning. Other end uses for sulphuric acid include: effluent/water treatment, plasticisers, dyestuffs, explosives, silicate for toothpaste, adhesives, rubbers, edible oils, lubricants and the manufacture of food acids such as citric acid and lactic acid.

Probably the largest use of sulphuric acid in which this chemical becomes incorporated into the final product is in organic sulphonation processes, particularly for the production of detergents. Many pharmaceuticals are also made by sulphonation processes.

1.2 Scope of this BAT Booklet

Many processes of sulphuric acid production have been developed according to the large number of sources of raw materials (SO_2), and their specific characteristics. The present document deals also with the production of oleum. It is possible to draw a general diagram of sulphuric acid production distinguishing the two fundamental steps of the process (see Figure 1):-

- Conversion of SO_2 into SO_3
- Absorption of SO_3

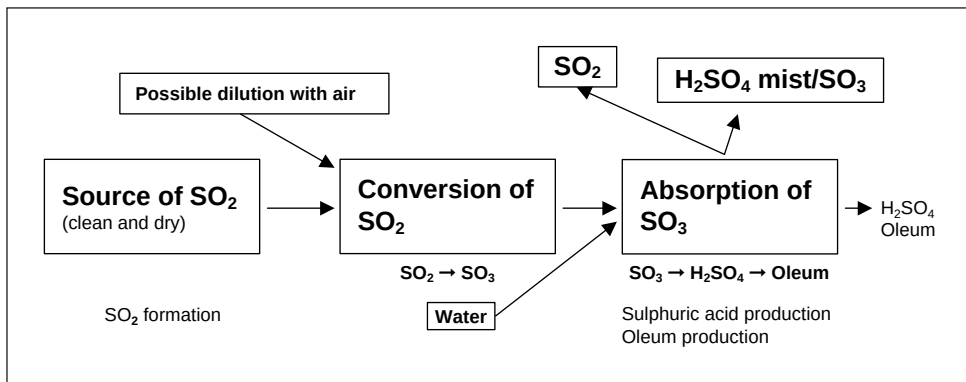


Figure 1 – General Diagram of Sulphuric Acid Production.

2. APPLIED PROCESSES AND TECHNIQUES

2.1 Raw Material Preparation including Storage and Handling

2.1.1 Sulphur storage and handling

Liquid sulphur is a product of the desulphurisation of natural gas and crude oil by the Claus-Process, with the cleaning of coal flue gas as a second source. The third way is the melting of natural solid sulphur (Frash-process) but this is not in frequent use because there are many difficulties in removing the contaminants.

The following is a typical analysis of molten sulphur (quality: bright yellow):-

Ash	max. 0.015% weight
Carbon	max. 0.02% weight
Hydrogen sulphide	ca. 1-2mg.kg ⁻¹
Sulphur dioxide	0mg.kg ⁻¹
Arsenic	max. 1mg.kg ⁻¹
Mercury	max. 1mg.kg ⁻¹
Water	max. 0.05% weight

Liquid sulphur is transported in ships, railcars and trucks made of mild steel. Special equipment is used for all loading and unloading facilities. Liquid sulphur is stored in insulated and steam heated mild steel tanks. The tank is equipped with submerged fill lines to avoid static charges and reduce agitation in the tank. The ventilation of the tanks is conventionally free. A further fact is less de-gasing of hydrogen sulphide and sulphur dioxide. All pipes and pumps are insulated and steam heated. The normal temperature level of the storage and handling is about 125-145°C.

2.1.2 Ore storage and handling

2.1.2.1 Pyrites

Normally pyrites is produced in a flotation process, which means that the concentrate is relatively finely ground with a moisture content dependent on how much energy is spent in the drying step. The analyses are variable within following ranges:-

Table 3 Range of Analyses of Pyrites

Element		Content	Content in one specific pyrite
Sulphur	weight %	30-52	50-52
Iron	weight %	26-46	45
Copper	weight %	up to 2.7	max. 0,10
Zinc	weight %	up to 3.0	max. 0,10
Arsenic	weight %	up to 10.0	max. 0,06
Water	weight %	5-9	5

A number of other metals are present in small quantities. The right hand column shows the analyses of one certain pyrite.

Pyrites should be covered during storage and transport to avoid dust. Outside storage can give rise to two problems depending on the climate:-

- Dust problems can be expected under dry conditions. A dusty atmosphere, especially inside buildings can cause a fire or an explosion under the right conditions
- Water in contact with pyrites becomes acidic under wet conditions. This water has to be removed and treated before loading for transport to the recipient. With too high a moisture content the pyrites will give clogging problems in the internal transport system at the plant

2.1.2.2 Metal sulphide ores

Approximately 85% of primary copper is produced from sulphur ores and therefore sulphur is a by-product of the majority of copper processes. Copper ore concentrates are produced in the flotation process and consist mainly of copper pyrites or chalcopyrite (CuFeS_2) but may also contain pyrites, chalcocite, bornite, cuprite and other minerals. A typical concentrate composition is 26-30% Cu, 27-29% Fe and 28-32% S.

Copper concentrates are usually processed by pyrometallurgical methods. Ores and concentrates are delivered to site by road, rail or ship. Copper concentrates are usually stored in closed buildings. Silo systems are used for the intermediate storage and preparation of the blend. Dust collection and abatement systems are used extensively during the unloading, storage and distribution of solid material.

Zinc and lead are for a major part, produced from sulphur ores and thus sulphuric acid is also a final product of treating these ores in metallurgical processes. In the first step the basic ores are treated in a flotation process to become concentrates, which are then shipped to Smelters for metal recovery. The concentrates are usually processed by metallurgical methods to remove sulphur. Ores and concentrates are delivered to site by road, train or ship.

The storage on site may be in the open air or in covered buildings depending on local conditions. In every case silo systems and dust collection systems such as bag filters are used to avoid dust propagation during intermediate storage in the process and the preparation of the blend.

2.1.3 Organic spent acids

Spent acids from different operations such as steel pickling, titanium dioxide production or organic sulphonation reactions have such a variety of compositions that it is not possible to define a set of general rules for preparation, storage and handling. Each case must be treated individually with special consideration given to dilution and any impurities which may affect all operations. Experience and know-how are of paramount importance.

Spent acids come mainly from organic chemical production. Sulphuric acid is mostly used as a catalyst and needs to be replaced with fresh concentrated acid when diluted and/or saturated with organics. Alkylation processes in refineries and nitration and sulphonation

processes in the chemical industry generate large amounts of spent acids which, after regeneration, become clean acid which can be recycled in any process.

Spent acids can be received by barges, road and rail tankers. Chemical analysis and physical tests are carried out before unloading to be sure the product meets the acceptance contract and to avoid any chemical reaction in storage when mixing spent acids from different processes. Storage vessels are banded. The storage gas phases are connected to the thermal decomposition furnace through non flammable systems on account of the risks due to the organics vapour pressure, to some dissolved sulphur containing products and to potential NO_x emissions. Nitrogen is used to blanket the gas phase to avoid any oxygen intrusion. Materials of construction depend on the strength of the spent acid. Corrosion resistant pumps and pipes are used for the feeds to the furnace.

2.1.4 H₂S or other sulphur containing gases

Off-gases containing H₂S and CS₂ are formed during the production of textile fibres, which are made in the viscose process. Off-gases containing H₂S or SO₂, depending on the process, are formed during the production of synthesis gas using fuel oil as a feedstock.

2.1.5 SO₂ gases from different sources

Gases containing up to 90% SO₂ from the production of organic compounds such as sulphonates and sulphites or from the combustion of gases containing H₂S, can be used as a source of SO₂ after the separation of organic compounds.

2.1.6 Sulphate salts

Ferrous sulphate is obtained in large quantities as its heptahydrate (FeSO₄.7H₂O) during the regeneration of pickling liquors or as a side product in the TiO₂ process via the sulphate route.

2.2 Material Processing

2.2.1 Conversion of SO₂ into SO₃

The design and operation of sulphuric acid plants are focused on the following gas phase chemical equilibrium reaction with a catalyst:-



This reaction is characterised by the conversion rate, which is defined as follows:-

$$\text{conversion rate} = \frac{\text{SO}_2 \text{ in} - \text{SO}_2 \text{ out}}{\text{SO}_2 \text{ in}} \times 100 (\%)$$

Both thermodynamic and stoichiometric considerations are taken into account in maximising the formation of SO₃. The Lechatelier-Braun Principle is usually taken into account in deciding how to optimise the equilibrium. This states that when an equilibration system is subjected to stress, the system will tend to adjust itself in such a way that part of the stress is relieved. These stresses are, for example, a variation of temperature, pressure, or the concentration of a reactant.

For SO_2/SO_3 systems, the following methods are available to maximise the formation of SO_3 :-

- Removal of heat – a decrease in temperature will favour the formation of SO_3 since this is an exothermic process
- Increased oxygen concentration
- Removal of SO_3 (as in the case of the double absorption process)
- Raised system pressure
- Selection of the catalyst to reduce the working temperature (equilibrium)
- Increased reaction time

Optimum overall system behaviour requires a balance between reaction velocity and equilibrium. However, this optimum also depends on the SO_2 concentration in the raw gas and on its variability with time. Consequently, each process is more or less specific for a particular SO_2 source.

2.2.2 Absorption of SO_3

Sulphuric acid is obtained from the absorption of SO_3 and water into H_2SO_4 (with a concentration of at least 98%).

The efficiency of the absorption step is related to:-

- The H_2SO_4 concentration of the absorbing liquid (98.5-99.5%)
- The range of temperature of the liquid (normally 70°C - 120°C)
- The technique of the distribution of acid
- The raw gas humidity (mist passes the absorption equipment)
- The mist filter
- The temperature of incoming gas
- The co-current or counter-current character of the gas stream in the absorbing liquid

SO_3 emissions depend on:-

- The temperature of gas leaving absorption
- The construction and operation of the final absorber
- The device for separating H_2SO_4 aerosols
- The acid mist formed upstream of the absorber through the presence of water vapour

2.3 Product Finishing

2.3.1 Dilution of absorber acids

The acid produced, normally 95.5%-96.5% or 98.5%-99.5%, is diluted with water or steam condensate down to the commercial concentrations: 25%, 37%, 48%, 78%, 96% and 98% H_2SO_4 . The dilution can be made in a batch process or continuously through in-line mixing.

2.3.2 SO₂-Stripping

A small amount of air is blown through the warm acid in a column or tower to reduce the remaining SO₂ in the acid to < 20mg SO₂.kg⁻¹. The air containing SO₂ is returned to the process.

2.3.3 Purification

Sulphuric acid from the start up of acid plants after long repair may be contaminated and clouded by insoluble iron sulphate, or silicate from bricks or packing. The acid can be filtered using conventional methods. Filter elements are required in the filling lines for tanker or rail-way loading to maintain quality.

2.3.4 Denitrification

A number of different methods are used for the denitrification of sulfuric acid and oleum. Various chemicals are used to reduce nitrosylsulphuric acid (NOHSO₄) or nitrate to N₂ or N_xO_y (See Table 4). The reactant must be added in stoichiometric amounts.

Table 4 Methods of Denitrification

Method of denitrification	Special conditions	Effect	In tail gas
Urea	Absorber/tanks	+/only <80% acid	N ₂
Dihydratedisulphate 40%	Absorber/tanks	+++/-acid and oleum	N ₂ , N ₂ O
Amidosulphonic acid 15% Hydroxylammoniumsulphate	Absorber/tanks	+++/-only 50-99.5% acid	N ₂
SO ₂ saturated acid	78% H ₂ SO ₄ / separated tower	+++/-only acid/ water balance	NO _x

2.3.5 Decolourisation

Acid produced from smelter plants or from acid regeneration plants can contain hydrocarbons or carbonaceous material, which is absorbed in sulphuric acid. This causes a ‘black’ colour. The decolourisation is known as “acid bleaching”.

Method of decolourisation	Special conditions	Effect
Hydrogen peroxide solution <60%	Absorber/tanks	+++/-acid and oleum

2.4 Use of Auxiliary Chemicals/Materials

2.4.1 Catalysts

When producing sulphuric acid by the contact process an important step is to produce sulphur trioxide by passing a gas mixture of sulphur dioxide and oxygen over a catalyst according to the equation:-



Without a catalyst this reaction needs a very high temperature to have a realistic rate. The equilibrium is however in favour of SO_2 – formation at higher temperatures which makes the conversion very poor.

Of all substances tested for catalytic activity toward sulphur dioxide oxidation only vanadium compounds, platinum and iron oxide have proven to be technically satisfactory. Today vanadium pentoxide is used almost exclusively.

Commercial catalysts contain 4-9 wt % vanadium pentoxide, V_2O_5 , as the active component, together with alkali metal sulphate promoters. Under operating conditions these form a liquid melt in which the reaction is thought to take place. Normally potassium sulphate is used as a promoter but in recent years also caesium sulphate has been used. Caesium sulphate lowers the melting point, which means that the catalyst can be used at lower temperatures. The carrier material is silica in different forms.

The catalyst components are mixed together to form a paste and then usually extruded into solid cylindrical pellets, rings or star-rings which are then baked at elevated temperatures. Ring (or star-ring) shaped catalysts, which are mostly used today, give a lower pressure drop and are less sensitive to dust blockage.

The lower temperature limit is 410-430°C for conventional catalysts and 380-390°C for caesium doped catalysts. The upper temperature limit is 600-650°C above which, catalytic activity can be lost permanently due to reduction of the internal surface.

The average service life for the catalyst is about 10 years. Service life is generally determined by catalyst losses during the screening of the catalyst which is necessary from time to time to remove dust [1], [2].

2.5 Intermediate and Final Product Storage

There is no air pollution problem connected with the storage, handling and shipping of sulphuric acid because of the very low vapour pressure of H_2SO_4 in normal temperature conditions. The handling of pure SO_3 and oleum requires safety procedures and management in order to avoid atmospheric pollution in the case of an accidental release.

Important considerations with regard to the ancillary operations referred to above, are as follows:-

- The receipt, handling and storage of powdered raw materials should be carried out so as to minimise the emission of dust. Liquid and gaseous feeds should be carefully contained to prevent the emission of odorous fumes or gases
- Oleum and SO_3 storage and handling operations, which are often linked with H_2SO_4 production, should be installed with a means of controlling fume emissions. Venting should be directed towards acid tanks or scrubbing systems. Installations should be built by following the best engineering practice. The emissions can condense and solidify in cool areas so this must be very carefully guarded against to prevent over-pressurisation of storage tanks

- During storage and handling of sulphuric acid, leaks may have an impact on the soil or on waters. Precautions have to be taken in order to reduce the possibility and the gravity of these leaks. See reference [3] for the minimum requirements

2.6 Energy Generation/Consumption, Other Specific Utilities

The process steps: burning sulphur, roasting sulphidic ores, SO_2 conversion and SO_3 absorption are exothermic processes. This means that from a technical point of view, installations for removing energy are of great importance for the production of sulphuric acid. This is coupled most effectively with energy winning in different levels and forms. Energy winning is dependent on the process strategy for the target products, for the local conditions, and for a possible relationship to other production processes. The age of the production units is more important than energy generation/consumption because materials of construction and specific buildings fix the technical possibilities for energy optimisation. A sulphur burning process in conjunction with double absorption is the most energy efficient.

The different energy-winning techniques are:-

- All techniques of steam generation as used in electrical power generation with special apparatus such as super-heater, economiser or steam boiler for sulphur burning
- Steam generation by the inter-pass absorption with temperatures from 110°C to 180°C and steam pressures from $1.5\text{bar}_{\text{abs}}$ to $11\text{bar}_{\text{abs}}$
- Steam turbines with power generation up to 15MWh ($1,250\text{t.d}^{-1}$ 100% H_2SO_4 Plant)
- Water preheating in the end absorption from 40°C to 80°C

Special programs are used for the optimisation of the process (e.g. cost savings and winning energy).

An essential characteristic of a conventional cold-gas plant (metallurgical gases) is that almost all the energy is discharged as waste heat at low temperature. Double absorption processes based on metallurgical gases, differ from hot-gas plants based on sulphur combustion in that cold feed gases must be heated to the converter-inlet temperature using the energy liberated in the oxidation of sulphur dioxide. See Appendix.

At a feed-gas concentration of 8.5% SO_2 and a dryer inlet temperature of $30\text{--}40^\circ\text{C}$ about 2.7GJ of thermal energy is liberated per tonne of sulphuric acid (5.4GJ in the case of sulphuric acid produced from elemental sulphur). This corresponds to a thermal output of 31 Mw for a $1,000\text{t.d}^{-1}$ plant. About 45% of the total energy is discharged through the intermediate absorber acid cooling system, 23% through the final absorber acid cooling system and about 22% through the dryer-acid cooling system.

In terms of heat recovery, in a conventional cold-gas double-absorption plant for processing relatively low-grade sulphur dioxide containing feed gases, there is no excess high temperature heat that can be used for the generation of high pressure steam. However, where the sulphuric acid plant is linked to a modern smelter, high SO_2 is available and to increase the output of high pressure steam, low temperature heat from the absorber acid circuits can be used for preheating the boiler feed water.

2.7 Gas Cleaning of Metallurgical Off-gases

Gases containing SO_2 from all metallurgical processes are cleaned before the contact process to remove the following components:-

- Fumes or aerosols formed by condensation of volatile metal components such as Zn, Pb, Sb, Bi, Cd and their chlorides, sulphates and oxides
- Volatile gaseous metals such as As, Se, Hg and their compounds
- Gaseous non-metallic compounds such as HF, HCl, SO_3 , CO

After cleaning, small amounts of impurities are absorbed in sulphuric acid or emitted with the tail gas through the stack. CO is oxidised to CO_2 in the contact process and gases from combustion processes also contain CO_2 .

Table 5 shows the different metallurgical off-gases, the main disposals and the method of cleanup.

Table 5 Disposal and Clean-up of Metallurgical Off-gases

Off-gas from	Main disposal	Cleanup system
“CuS” smelters	Hg, HF	ESP, Gas scrubber with HgCl_2 or $\text{Na}_2\text{S}_3\text{O}_3/\text{HgS}$
“PbS” smelters	Hg	ESP, Gas scrubber with HgCl_2
“ZnS” smelters	Hg	ESP, Gas scrubber with HgCl_2
“Ni” smelters	Se	Gas scrubber

2.8 Handling of Waste Gas/Stack Height

The height of the exhaust stack determines the maximum SO_2/SO_3 concentration value in the ambient air surrounding a sulphuric acid plant. It is also well known that this concentration is widely fluctuating in space and time due to the thermo-aerodynamic conditions of the low-level atmosphere (0 to 500m). These conditions can vary due to the following factors:-

- Vertical temperature and humidity structure
- Wind speed and direction
- Turbulence of the atmosphere
- Sunshine intensity etc.

Proposals for stack heights could consequently have a questionable character.

For the time being, every Member State has its own method for estimating the height of stacks. In the future, it is foreseen that a specific Technical Note on this topic will be published by the European Commission.

3. PRESENT CONSUMPTION/EMISSION LEVELS

3.1 Consumption of Energy/Raw Materials/Water Input and Waste

The Appendix gives typical inputs/outputs for different types of a 4-bed contact process per tonne 100% H_2SO_4 .

The types of process are:-

- Sulphur-burner, pyrites roasting, “CuS” roasting, “ZnS” roasting, “PbS” roasting
- H_2SO_4 regeneration, “ FeSO_4 ” roasting

3.2 Emission Levels

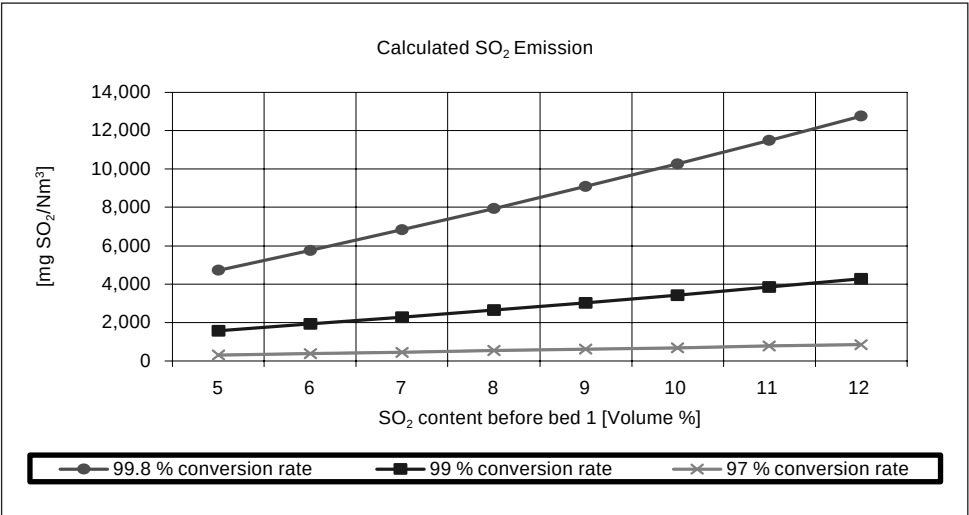


Figure 2 – Calculated SO_2 Emissions in mg.Nm^{-3} in Relation to the SO_2 Content before Bed 1.

3.3 Environmental Aspects

3.3.1 Emissions into air/water, waste generation

3.3.1.1 Emissions into air CO_2 , SO_x , NO_x

3.3.1.1.1 SO_3 emissions

Origins:-

- Bad absorption efficiency
- Vapour pressure of sulphuric acid/oleum

Minimisation techniques:-

Absorption improvements:-

- Absorbing tower design (velocity)
- Acid distribution (flow and repartition)
- Packing efficiency
- Acid temperature (vapour pressure)

3.3.1.1.2 H_2SO_4 emissions

Origins:-

- Tower design
- Mist formation
- Vapour pressure

Minimisation techniques:-

- Droplet carry-over
- Absorbing tower design (gas velocity, acid distribution)/demisters (mesh pads or candles)
- Mist filter
- Process control:-
 - ESP efficiency
 - Drying tower efficiency
 - Gas temperature upstream absorption
 - NO_x content in the gases
 - Acid temperature at the bottom of absorption tower
 - Acid vapour pressure (temperature)
 - High Efficiency demisters $\rightarrow 50\text{mg.Nm}^{-3}$ (particles $> 0.5\mu$)

3.3.1.1.3 SO_2 emissions

Origins:-

- Bad conversion efficiency
- Gas bypassing (acid cross bleed or convector)

Minimisation techniques without additional process:-

Gases:-

- Composition (O_2 , SO_2 , inerts...)
- Velocities through catalyst and repartition
- Cooling quality (heat exchangers or air cooling)
- Operating pressure
- Acid cross-bleeds (SO_2 stripping, SO_2 gases drying processes)
- Temperature

Catalyst:-

- Converter design
- Number of beds
- Catalyst quality and quantity
- Converter loading

SO_2 -Minimisation techniques with additional process:-

- Without by-product: Single absorption $\rightarrow$ double absorption (if gases are higher than 6% SO_2)
 - $\text{SO}_2 \rightarrow$ weak H_2SO_4 possible to recycle: Activated carbon oxidation process/ H_2O_2 process
- With co- or by-product:-
 - NH_3 scrubbing, Co product $\rightarrow$ Ammonium sulphate
 - NaOH scrubbing, Co product $\rightarrow$ Sodium sulphate
 - $\text{Ca}(\text{OH})_2$ scrubbing, Co product $\rightarrow$ Calcium sulphate (gypsum)
 - $\text{Mg}(\text{OH})_2$ scrubbing, Co product $\rightarrow$ Magnesium sulphate
 - Other processes – neutralisation absorption, bioconversion – exist but are less developed and depend on the specific site

3.3.1.2 Emissions into water

- Energy release from cooling
- Accidental leakage
- Waste water treatment plants must be able to deal with heavy metals
- Emissions of noise by air cooling
- Water treatment for steam production

3.3.1.3 Solid wastes

3.3.1.3.1 Sulphuric acid spent catalysts

Methods for disposing of spent catalyst are:-

- Metal recovery

The vanadium content of the catalysts can be reclaimed for further use. This service is usually provided by the catalyst manufacturer who will have access to a reclamation operation. The metal can be recycled as vanadium salts or as ferrovanadium for steel production.

In all cases of the recycling versions it is very important that the spent catalyst has a low content of arsenic. A typical analysis for spent catalyst:-

V₂O₅: min. 3% weight

K₂O: max. 10% weight

P: max. 0.5% weight

Sn, Pb, As, Sb, Bi, Cu, Zn, Cd, Hg: max. 0.1% weight

- Landfill Disposal:-

Two types of disposal are available

Fixation: The catalyst is ‘fixed’ in an inert matrix, usually concrete or glass (also known as vitrification) prior to controlled deposit in a suitably licensed landfill site. The fixation process is designed to prevent metals leaching into the landfill site.

Direct landfilling: The catalyst is deposited directly into a suitably licensed landfill site in compliance with national legislation. It is common practice to mix the catalyst with lime to neutralise residual acidity.

3.3.1.3.2 Wastes from packing and lining

Waste from the chemical industry is always handled with care. Waste from sulphuric acid production, packing, lining and scrap-iron is always handled in the same way as waste from other chemical production plants. That means that where it is necessary, the waste is checked for impurities before a decision is made on how to handle it. There are usually no problems in normal sulphuric acid production

3.3.2 Consumption of water/energy and other resources

Sulphuric acid production is one of the few chemical processes where more energy is normally produced than is used in the process. In many cases sulphuric acid plants are used as the energy source for the production processes for other chemicals that require energy. The Appendix shows the energy outputs from different plants.

Sulphuric acid production also has the advantage that there is no formation of carbon dioxide compared with fuel and natural gas and energy is “green” compared to other energy production due to the fact that the energy is a by-product. Overall the process is a net producer of energy, although the amount of recovery is a function of the level of quality of this energy.

3.3.2.1 Consumption of water

All acid plants have measures to control the use of water for cooling and adjusting the concentration in the acid system. The cooling system is normally a closed water circuit or it includes a measurement of the pH before discharge to waste. The use of water in the acid system is important to ensure the right concentration in the absorption tower to prevent acid mist in the stack.

Boiler feed water for steam production requires special pre-treatment depending on the different sources such as ground water or drinking water. Treatments include anion and/or cation exchange and conditioning with ammonia, sodium hydroxide, hydrazine or phosphates. Water quality including pH and conductivity must be fully controlled. About 95% of the water is used for steam production and the remainder of the boiler water which is mostly alkaline can be discharged to drain after neutralisation. In the interests of economy all uncondensated water condensates should be collected and used for new steam production.

3.3.2.2 Energy consumption

Sulphuric acid production is always a net producer of energy. The quality of the energy produced is a function of site requirements. Examples of the different kinds of energy produced are: steam at different pressures for chemical plants, power generation or city heating; or hot water for use in greenhouses or fish farms.

3.3.2.3 Other resources

Regeneration, recycling and evaporation are different ways to prevent spent acid becoming a waste and a problem for the environment. A sulphuric acid plant to process the tail gas from metal roasting prevents the emission of sulphur dioxide to the atmosphere.

3.3.3 Accidental pollution

There is always a risk of accidental pollution when chemicals are produced and handled. The more common a chemical, the more information is available about the different hazards and the lower the risk of accidental pollution. The highest risk for accidental pollution is during the transportation of the product and that is covered under the different transport regulations such as those of ADR/RID and IMO. There is also a risk of pollution from the storage of sulphuric acid and different plants have different systems to collect leaks and spillages depending on guidelines for the storage of acid.

Gas leaks are not normally a problem as they are handled by various monitoring and control systems, which measure the SO₂ content in the air.

3.3.4 Areas of concern

The most important issue is the transportation of the product and that is covered under the regulations of ADR/RID and IMO. There is a risk to personnel during the loading and unloading of sulphuric acid if it is mishandled. All producers are responsible for the personal safety of their employees and have different systems of work to ensure proper handling.

3.3.5 Multimedia complexity

Emissions of sulphur dioxide into the air may deposit on the soil and contribute to a lower pH.

SO₂ scrubbing gives rise to a by-product disposal problem which will depend on the type of by-product. For example gypsum may be disposed of to landfill and ammonium sulphate may be sold or recycled.

4. CANDIDATE BATS

4.1 Available Techniques

The general presentation of the technique of production of sulphuric acid is divided into two parts as the techniques for the conversion of SO₂ to SO₃ and of absorption of SO₃ depend on the concentration of SO₂ in the feed gas entering the installation and on the variability of SO₂ concentration.

Sources of SO₂

- Sulphur burning
- Pyrites roasting
- Metal sulphide roasting and smelting
- Sulphuric acid regeneration
- Metal sulphate roasting
- Combustion of H₂S or other sulphur containing gases
- Other processes

Sulphuric acid production

Acid production is divided into two different groups depending on the level of SO₂ in the process gas.

Poor gas processes with > 3 Vol. % SO₂:-

- Single contact process
- Double contact process
- Wet Contact Process (WCP)

Tail gas processes with < 3 Vol. % SO₂:-

- Modified Lead Chamber Process (MLCP)
- H₂O₂ process
- Activated Carbon
- Other processes

4.1.1 Overview of techniques applicable to sources of SO₂

Figures 3.1 to 3.6 in the Appendix detail the characteristics of the principal sources of SO₂ dependent on the different processes. Table 6 gives an overview of techniques that have a positive effect on, that is reduce, the emissions from the manufacture of sulphur dioxide.

Table 6 Techniques Reducing the Emissions

Techniques	Process control	Fuel selection	ESP	Filters	SO _x
Sulphur burning	X			X	X
Ore roasting/smeltering	X	X	X	X	X
H ₂ SO ₄ Regeneration	X	X	X	X	X
Sulphate roasting	X	X	X	X	X
Combustion of H ₂ S	X	X		X	X

4.1.1.1 Combustion of Sulphur

The combustion of sulphur which is obtained either from natural deposits or from de-sulphurisation of natural gas or crude oil, is carried out in one-stage or two-stage sulphur combustion units at between 900 and 1800°C. The combustion unit consists of a combustion chamber followed by a process gas cooler. The SO₂ content of the combustion gases is generally up to 18% by volume and the O₂ content is low (but higher than 3%).

The gases are generally diluted to 10-11% before entering the conversion process. In the inlet gas to the converter the ratio SO₂/O₂ should not be higher than 0.8 to achieve a high conversion efficiency. This means that the highest percentage of SO₂ should not exceed 11% in a 4-bed double contact (no caesium) plant to achieve an average conversion rate of 99.6%.

4.1.1.2 Pyrites roasting

Fluid-bed roasters are the preferred equipment for pyrites roasting. They are much superior to other types of equipments in terms of process technology, throughput rates and economy. Two by-products, iron oxide and energy are also produced when roasting pyrites to get SO₂ gas. 1 tonne of acid needs 0.5 tonnes of pyrites. The SO₂ content of the gases is generally between 6 and 14% with zero O₂ in the gas. The SO₂ content in the gases is slightly variable over time due to the heterogeneous character of the raw material (pyrites).

The gases are always treated in 3-4 cleaning steps using cyclones, bag filters, scrubbers and electrostatic precipitators with a high efficiency. Waste water from the scrubbing must be treated before discharge. The clean gas is diluted with air to 6-10% and dried before entering the conversion process.

4.1.1.3 Metal sulphide roasting/smelting

Many metal sulphides (other than pyrites) produce gases containing SO_2 , when roasted during metallurgical processes. It is necessary to distinguish the main ores as indicated in Table 7.

Table 7 Principal Metal Sulphides Producing SO_2

Metal Sulphide	SO_2 %	Raw Gases O_2 %	Process Gases SO_2 %	Variability in time
ZnS containing ores	6-10	6-11	6-10	Relatively low
CuS containing ores	1-20	8-15	1-13	Can be very high
PbS containing ores				
– sintering	2-6	≈ 15	2-6	Relatively high
– other lead smelters	7-20	≈ 15	7-13	Low to very high (Batch process)

The concentration of SO_2 in gases entering an acid plant determines the amount of gas that must be treated per tonne of fixed sulphur. The size of the plant and the cost of fixing the sulphur increase as the concentration of SO_2 diminishes. Furthermore, there is a minimum concentration of SO_2 that can be treated without increasing the number of stages in the plant.

For copper, it is typical to find fluctuations in the concentration of SO_2 in converters and also important fluctuations in the gas flow. The reason for these effects is that about 30% of converter operating time is used for charging and slag tapping.

4.1.1.3.1 Copper production

Pyrometallurgical copper extraction is based on the decomposition of complex iron-copper sulphide minerals into copper sulphides, followed by selective oxidation, separation of the iron portion as slag, and final oxidation of the remaining copper sulphide. These steps are known as roasting, smelting and converting (the present-day tendency is to carry out the first two in a single process). The Flash Smelting process is currently one of the most widely used pyrometallurgical processes.

Converters are used extensively to blow air, or oxygen-enriched air, through the copper matte to produce blister copper. Virtually all the sulphur from the concentrates is converted to SO_2 . A concentrate of CuFeS_2 produces almost one tonne of sulphur (2 tonnes of SO_2) per tonne of copper extracted. To avoid air pollution, these gases are processed to obtain sulphuric acid, oleum or liquid SO_2 .

The development of copper recovery processes has been dominated by two objectives. One is to economise on energy, making the maximum use of reaction heat obtained from the processes. The other has been the need to decrease the gas volume and increase the concentration of SO_2 in metallurgical gases by the use of oxygen enrichment, to improve environmental controls. The gas purification follows, during which the gas is cooled and the dust and contained SO_3 are eliminated by scrubbing, cooling and electrostatic cleaning. After that, the clean SO_2 gases are converted to sulphuric acid through the contact process.

4.1.1.3.2 Zinc production

Zinc production is based on the treatment of zinc concentrates, mainly sulphides, with an average composition of sulphide sulphur: 30-33%, Zn: 50-60%, Fe: 1-12%, Pb: 0.5-4% and Cu: 0.1-2%. These concentrates are desulphurised in a first step.

After the desulphurisation step the product (calcine) is treated for zinc recovery mainly in a hydrometallurgical process and for a minor part also in a pyrometallurgical process. The hydro way consists of leaching this calcine, purifying the enriched zinc solution and subsequently recovering pure zinc metal by electrolysis. In the pyrometallurgical way, conditioned calcine is reduced in a shaft furnace (ISF) and the zinc vapours are condensed in a splash condenser. This crude zinc is further refined in a distillation column.

More specifically, the preliminary desulphurisation step takes place mainly in a fluidised bed roaster or alternatively in a sinter plant. The SO_2 content of the gases is about 5 to 10%. After heat recovery in a waste heat boiler with the production of steam, the gases are dedusted by electrostatic precipitation (ESP), cooled down in scrubbing towers and subsequently demercurified in a specific scrubbing process. The cleaned SO_2 gases are treated and converted to sulphuric acid in a double contact process in modern plants or in a single contact process for older plants.

4.1.1.3.3 Lead production

Primary lead is produced predominantly from lead and lead/zinc concentrates and to a smaller extent from other sources, such as complex lead/copper concentrates. Concentrate compositions may therefore vary over a rather wide range: 10-80% Pb, 1-40% Zn, 1-20% Cu, 1-15% Fe, 15-35% S. Somewhat different processes have been developed and are used for an optimum recovery of the various metals present in the feed.

Whichever smelting technique is used, desulphurisation is always one of the objectives of the first treatment stages. It is carried out on belt sinter machines in those cases where a shaft furnace is the actual smelting step, or in flash or bath smelting furnaces in the other processes.

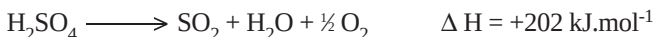
From this variety of feed materials and consequently of techniques, it should be clear that the characteristics of the SO_2 -containing gas will differ markedly from case to case. From continuous operations, such as sinter machines, the SO_2 -concentration can be kept fairly constant and depending on the actual feed mix it can be between 6 and 9%. From batch operations, it will vary between 0 and 15%, depending on the process stage. The average concentration may be between 2.5 and 10%, depending on the actual feed mix and the applied technique.

The gas cleaning circuit will always include ESP and scrubbers. Energy recovery can be practised in some cases of bath smelting but a specific mercury removal step, on the gas or on the acid, may be necessary in others. The double absorption process is largely used, particularly when SO_2 concentrations are high and constant. When low and very varying SO_2 concentrations are inevitable, or where those streams cannot be integrated in more steady gas streams from other processes on the site, single absorption is more appropriate.

4.1.1.4 Regeneration of sulphuric acid

Thermal decomposition of spent sulphuric acids to give sulphur dioxide is achieved in a furnace at temperatures around 1,000°C. Spent acids come from processes where H₂SO₄ or oleum is used as a catalyst (alkylation, nitration, sulphonation etc.) or from other processes where H₂SO₄ is used to clean, dry and remove water.

Gas phase thermolysis of sulphuric acid is represented by the overall equation:-



Spent acids are atomised in very small droplets to achieve a good thermal decomposition. Energy is provided by the organics from the spent acids and by additional energy from natural gas, fuel oil or coke. Preheating the combustion air reduces the amount of fuel needed. Furnaces can be horizontal (fixed or rotating) or vertical.

The SO₂ content in the gases mainly depends on the composition of the spent acids. The water and organics content affect the gas composition which can vary from 2 to 15%. Sulphur, pure or waste, can generally be added to adjust the SO₂ content and to try to avoid large variations. The most part of the energy from the combustion gases is recovered as steam in a Waste Heat Boiler. Downstream, the gases are cleaned, demisted and dried before going to the converter. The O₂/SO₂ ratio is important to get a conversion rate of SO₂ to SO₃ which is as high as possible. Upstream of the converter, the gases are reheated to the ignition temperature through gas/gas heat exchangers using the conversion heat. A double absorption process can be used only if the SO₂ content of the gases is high enough (about 8%) at the converter inlet.

Conversion rates:-

– Single absorption

SO ₂ content at the converter inlet	8%	with O ₂ /SO ₂ ratio of 1.1:	98%
SO ₂ content at the converter inlet	from 5 to 8%	with O ₂ /SO ₂ ratio of 1.1:	97 to 98%
SO ₂ content at the converter inlet	below 5%	with O ₂ /SO ₂ ratio of 1.1:	96 to 97%

– Double absorption

When achievable, double absorption leads to conversion rates from **99 to 99.6%**

Double absorption is considered as the BAT for new plants. For existing plants, a single absorption can be advantageously combined with an ammonia scrubber, the by-product obtained being either sold on the market or recycled in the furnace.

4.1.1.5 Sulphate roasting

Decomposition of sulphates, for example iron sulphate, is carried out in multiple-hearth furnaces, rotary kilns or fluid bed furnaces at over 700°C with the addition of elemental sulphur, pyrites, coke, plastic, tar, lignite, hard coal or oil as fuel compensator. The SO₂ content of the gases obtained is dependent on the type of fuel. After cleaning and drying, the SO₂ content is about 6% and the variability in time of the SO₂ content is high.

During the first step, the heptahydrate is dehydrated at 130-200°C by flue gases in spray dryers or fluid-bed dryers to a monohydrate or mixed hydrate. In a second step, the material is decomposed at about 900°C.

The gases thus obtained contain about 7% by volume of sulphur dioxide. Today it is common practice for ferrous sulphate to be decomposed in a fluid-bed pyrites roasting furnace at 850°C or more. Elemental sulphur, coal or fuel oil may be used as supplementary fuels. The sulphur dioxide containing gas leaving the furnace is cooled in a waste heat boiler to about 350-400°C and is subsequently passed to the gas cleaning system. The cleaned gases are fed to the sulphuric acid plant.

A mixture of sulphates (metallic or ammonium) and eventually sulphuric acid, resulting from the concentration of acidic wastes from titanium oxide production or from organic sulphonations, can similarly be processed in a fluid bed reactor or a furnace. In individual cases, ferrous sulphate is also decomposed in multiple-hearth furnaces with flue gases from fuel oil or natural gas combustion.

4.1.1.6 Combustion of sulphur containing gases

Combustion of hydrogen sulphide (H_2S) or similar gases is achieved in a fixed furnace at about 1000°C. Combustion heat is higher than with sulphur combustion. Two different ways are used to process the gases to SO_3 and H_2SO_4 :-

- A dry process where the water is eliminated by condensation and then drying and the gases are processed as in the spent acid regeneration process
- A wet process in which the gases are processed with all the water and steam. At the end of the process, the absorption tower is replaced by a condenser where the control of temperature allows the production of 96% H_2SO_4 , the most part of water being discharged to the atmosphere

The conversion rates are comparable to those for sulphur burning plants.

4.1.1.7 Tail gas scrubbing

SO_2 abatement by scrubbing consists of a chemical reaction between SO_2 and a basic liquid solution. This operation is achieved generally in a gas/liquid contact packed tower or a scrubber. A liquid circulation loop is operated from the bottom to the top of the tower, where the liquid is distributed above the packing.

The gases enter the bottom part of the tower, contact and react with the basic liquid solution on the packing. The SO_2 content in the outlet gases is achieved by controlling the pH of the solution and by adding more or less basic concentrated solution into the liquid circulation loop. One or two reaction steps may be needed depending on the inlet and outlet SO_2 content and the basic product used (ammonia, caustic soda, magnesium or calcium hydroxides, etc.). The resulting by-products (ammonium-, sodium-, magnesium-, or calcium-, sulphate, sulphite and bisulphite) can be sold or may have to be disposed of.

4.1.2 Overview of techniques applicable to sulphuric acid production

This section refers to existing plants which may (or may not) be up-graded, although not reaching the specifications of new plants.

4.1.2.1 Overview

The six process routes are the principal process routes that are available. The following data on production processes have been presented in detail in the previous paragraphs and are summarised in Table 8 using an O₂/SO₂ ratio of about 1 ± 0.2 (possibly 0.8 to 3).

Table 8 Sulphuric Acid Production Processes for New Plants

NEW PLANTS	SO ₂ content in feed gas (% vol)	Conversion rate daily average (%)	State of the art emission for new plants SO ₃ [2]
Single contact	6-10 3-6	98.5% [4] 97.5% to 98.5%	0.4kg.t ⁻¹ [5]
Double contact	6-12	99.6% [1]	0.1kg.t ⁻¹ [5]
Wet contact process	0.05-7	98.0%	< 10ppmv SO ₃
Process based on NO _x	0.05-8	nearly 100% [3]	No data
H ₂ O ₂ Process		> 99.0%	Very low

- [1] when sulphur burning
- [2] SO₃ + H₂SO₄ expressed as SO₃
- [3] possible emissions of NO_x
- [4] for existing plants the conversion rate is 98%
- [5] per tonne of acid produced

Table 9 gives an overview of techniques that have a positive effect on, that is reduce, the emissions from the manufacture of sulphuric acid

Table 9 Techniques Reducing the Emissions

Techniques	Process control	Single contact	Double contact	Catalysts	Filters	SO _x	NO _x
Sulphur burning	X		X	X	X	X	X
Ore roasting	X	X	X	X	X	X	
H ₂ SO ₄ regeneration	X	X	X	X	X	X	X
Sulphate roasting	X		X	X	X	X	
Incineration of H ₂ S	X	X	X	X	X	X	X

4.1.2.2 *Single contact process (single absorption)*

The contact process without intermediate absorption is only used in new plants to process SO_2 gases with low and widely varying SO_2 contents. The SO_2 -containing gases, which have been carefully cleaned and dried, are oxidised to sulphur trioxide in the presence of catalysts containing alkali and vanadium oxides. The sulphur trioxide is absorbed by concentrated sulphuric acid in absorbers, preceded by oleum absorbers where necessary. In the absorbers, the sulphur trioxide is converted to sulphuric acid by the existing water in the absorber acid. The absorber acid is kept at the desired concentration of approximately 99% by wt. by adding water or dilute sulphuric acid as shown in Figure 3.

The single contact process is generally used with inlet gases containing 3 to 10% SO_2 . In new plants, the conversion efficiency is about 98.5% as a daily average and can be upgraded to 99.1% depending on good design and the use of specially adapted catalyst doped with caesium. In existing plants, it is difficult to obtain better than 98.0% conversion but, in some existing plants, a conversion efficiency of 98.5% has been achieved.

4.1.2.3 *Double contact process (double absorption)*

In the double contact process, a primary conversion efficiency of 80% to 93%, depending on the arrangement of the contact beds and of contact time, is obtained in the primary contact stage of a converter preceding the intermediate absorber. After cooling the gases to approximately 190°C in a heat exchanger, the sulphur trioxide already formed is absorbed in the intermediate absorber in sulphuric acid with a concentration of 98.5 to 99.5% by weight. The intermediate absorber is preceded by an oleum absorber if required. The absorption of the sulphur trioxide brings about a considerable shift in the reaction equilibrium towards the formation of SO_3 , resulting in considerably higher overall conversion efficiencies when the residual gas is passed through one or two secondary contact beds. The sulphur trioxide formed in the secondary stage is absorbed in the final absorber.

The double contact processes including double absorption are shown in Figures 4, 5 and 6 with the different raw materials – sulphur, non-ferrous ores and pyrites. In general, SO_2 feed gases containing up to 12 Vol.% SO_2 are used for this process. The conversion efficiency in new plants can reach about 99.6% as a daily average in the case of sulphur burning.

4.1.2.4 *Wet contact process (WCP)*

This process is not sensitive to the water balance and has been used to treat off-gas from a molybdenum smelter as well as being installed in two desulphurisation plants (one in a Flue Gas Desulphurisation system, the other on an industrial boiler) currently under construction. An earlier version of the WCP technology was used to treat lean hydrogen sulphide gases. For all gas feeds, sulphurous components in the gas are converted to sulphuric acid without the need to dry the gas first. [33].

When treating roaster off-gas, the off-gas is cleaned in a standard purification system and then fed through a blower, which provides the pressure necessary to overcome the pressure

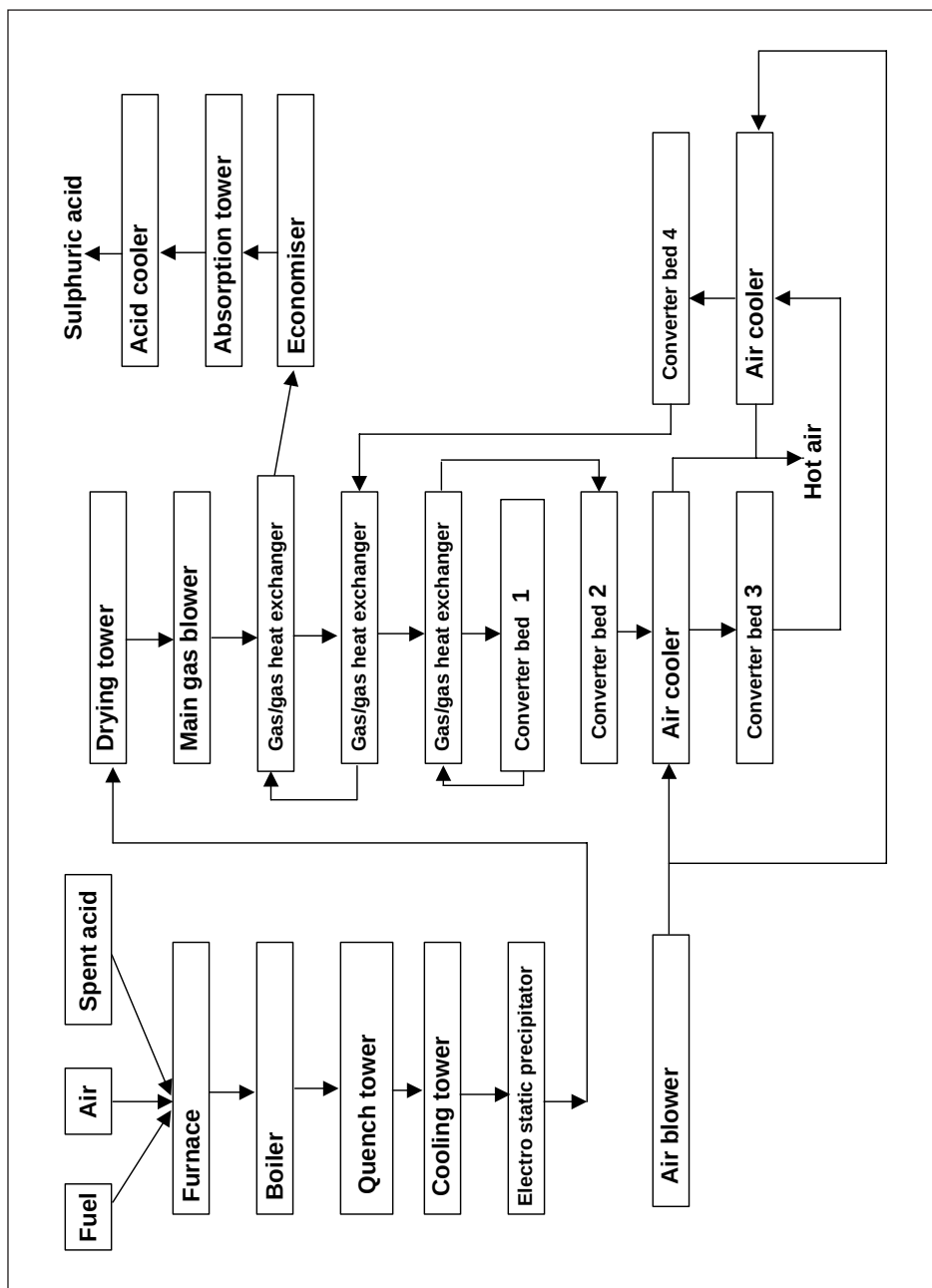


Figure 3 – Single Absorption Process for Spent Acid Regeneration.

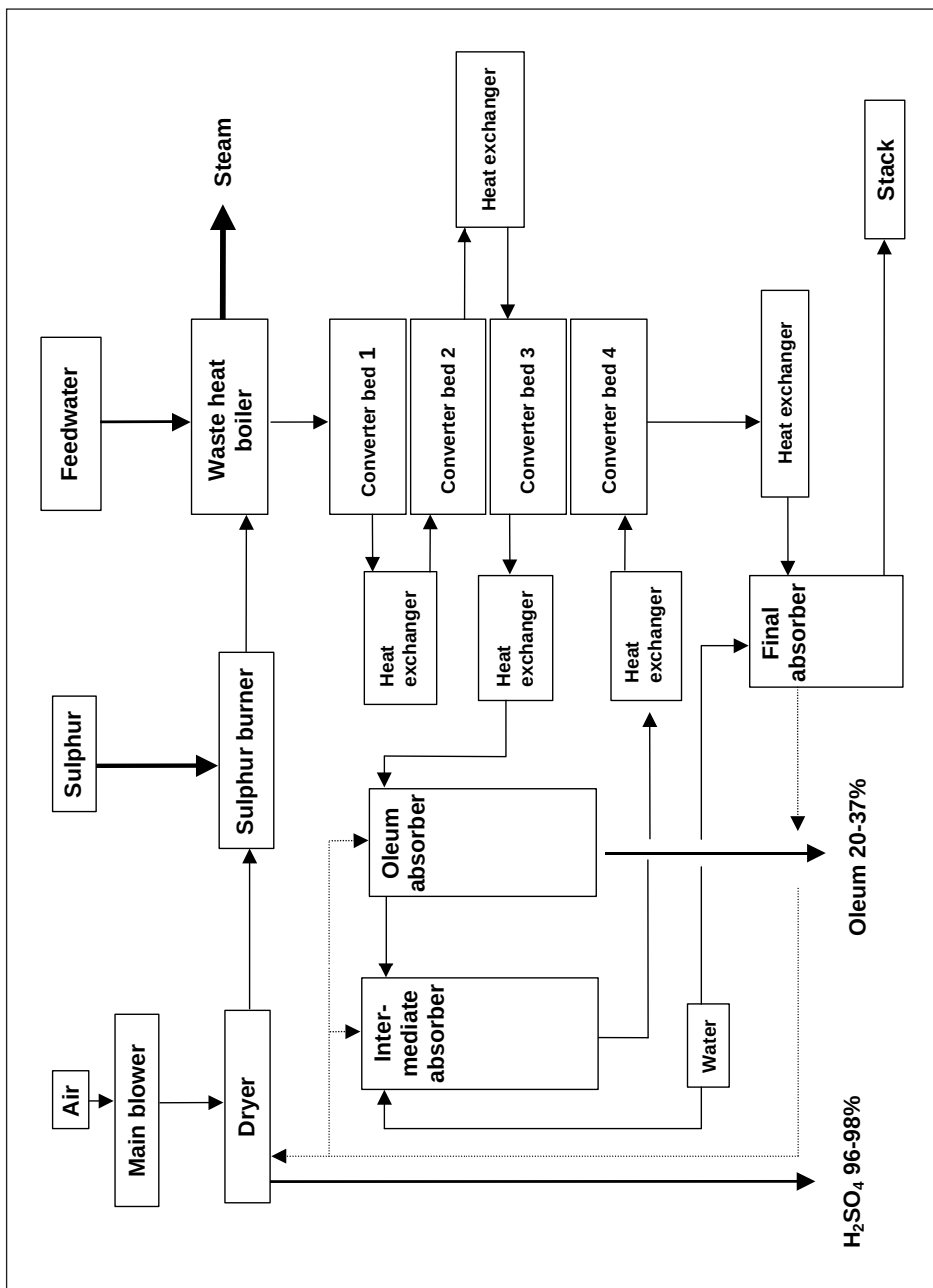


Figure 4 – Sulphuric Acid Plant (Double Catalysis) Based on Sulphur Combustion.

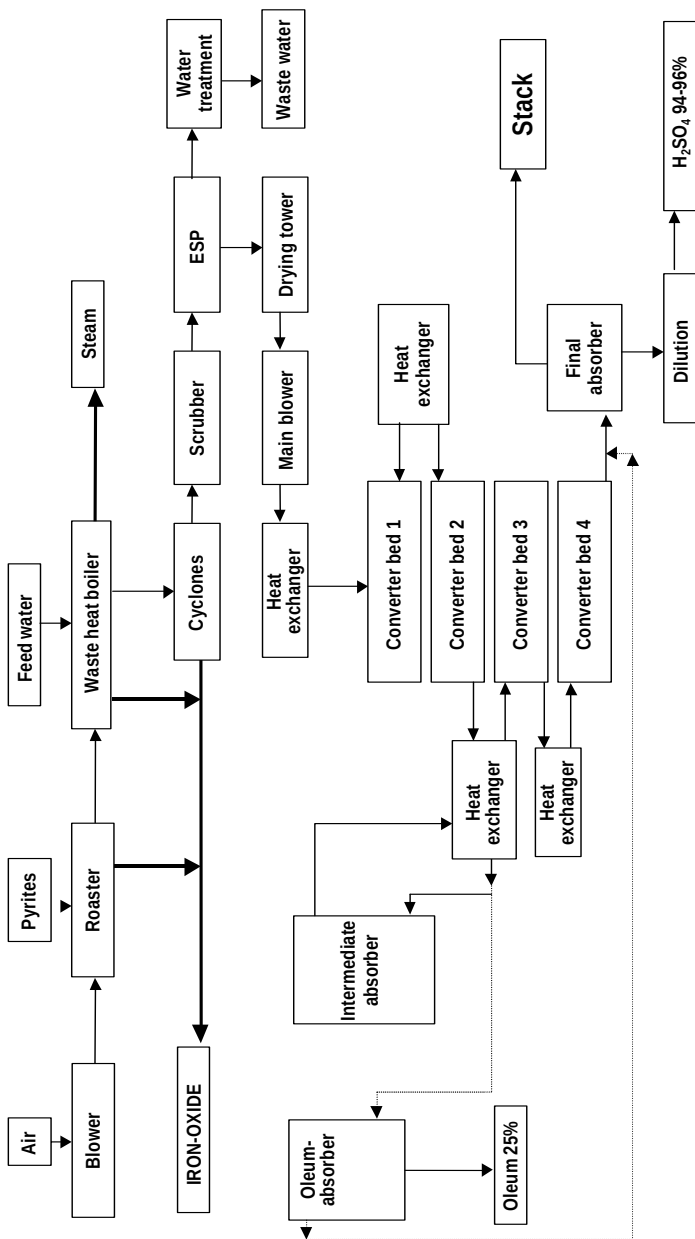


Figure 6 – Typical Layout of a Sulphuric Acid Plant (Double Catalysis) Based on Pyrites.

drop across the system. The gas is preheated initially in the tower and, secondly, in a heat exchanger. It is next fed to a converter, where sulphur dioxide is oxidised over a catalyst to sulphur trioxide. A cooled reactor or an adiabatic reactor is used, depending on the conditions.

Sulphur trioxide-containing gas is then cooled in a gas-gas heat exchanger. Consequently, part of the sulphur trioxide reacts with the water vapour in the gas to form sulphuric acid vapour. Finally, the sulphuric acid vapour is condensed and concentrated, without acid mist formation, in a multi-tube falling film condenser. Cooling is provided by the cold feed gas supplied to the shell side.

The only utilities required are cooling water for the acid coolers, electricity for the blower and fuel to enable autothermal operation if the feed gas contains below about 1.5-2.0% SO_2 . The conversion efficiency is about 98.5% as a daily average.

4.1.2.5 Pressure process

As the oxidation of SO_2 is favoured by pressure, Pressure Contact Processes have been developed in which the sulphur combustion, sulphur dioxide conversion and sulphur trioxide absorption stages are effected at elevated pressure. Several parameters can influence the conversion efficiency by modifying the chemical equilibrium. Pressure is one of these parameters and this displaces the equilibrium to the right. One plant in France, a double-absorption plant with a capacity of $550\text{--}575\text{t.d}^{-1}$ of H_2SO_4 , has been designed with the pressure process in the early 1970s and is still in operation. Usual sulphuric acid processes are operated at pressures in the range of 0.2 to 0.6bar.

Two special advantages have been claimed for the pressure contact process compared with the conventional double-absorption process:-

- The position of the chemical equilibrium in the sulphur dioxide oxidation reaction is more favourable, allowing a higher conversion efficiency to be attained with a reduced amount of catalyst. The plant is reported to have achieved 99.80-99.85% conversion. The tail gas sulphur dioxide content is reported to be reduced to about 200-250ppm SO_2 . However, the high temperatures in the sulphur furnace increase the rate of formation of nitrogen oxide
- Smaller equipment can be used because of the lower operating volumes of the converter gases. This reduces material and site area requirements and raises the capacity limit of shop-fabricated equipment. The resulting capital cost savings are said to be about 10-17% in comparison with current double-absorption plants. However, in some countries these savings would be nullified by the cost of conforming to the requirements for extra wall thickness and higher-grade materials of construction laid down in the safety regulations relating to pressure vessels

The principal disadvantages of the pressure contact process compared with the conventional double-absorption process is that it consumes more power and produces less steam.

4.1.2.6 Other processes

Other processes are defined as processes which yield sulphuric acid but which are not economically viable for large scale production for different reasons.

4.1.2.6.1 Unsteady state oxidation process

This new method of SO_2 oxidation is based on a periodic reversal of the direction of the reaction mixture flow over the catalyst bed. The process was developed at the Institute of Catalysis of the former USSR. Basically a large bed of catalyst is used as both a reversing, regenerating heat exchanger and as a catalytic reactor for the SO_2 oxidation reaction.

Cold SO_2 gas is fed into the catalyst bed and is heated to catalyst ignition temperature by the heat stored in the bed. At this point the conversion reaction proceeds, producing heat. The heat is absorbed by the catalyst in the bed, increasing its temperature. When the front comes close to the exit side of the bed, the flow through the reactor is reversed. Flow reversals are made every 30-120 minutes. The main advantage of the unsteady state process is that the operating line for the first bed is almost vertical, giving first bed conversion of about 80-90% at a low exit temperature. The process is auto-thermal at low (0.5-3%) SO_2 gas concentrations.

The process is in operation in several plants in Russia and other Eastern European countries.

4.1.2.6.2 H_2O_2 Process

The conversion of SO_2 to SO_3 can be achieved by the use of H_2O_2 at a sulphuric acid concentration of 70%. Conversion efficiency is higher than 99% but the cost of H_2O_2 makes this an expensive process for sulphuric acid production. However, since the process leaves no waste, it is very useful for tail gas scrubbing where especially difficult local conditions cannot tolerate the emission even from an installation as efficient as the best contact plant. The H_2O_2 is used either directly or is produced by electrolysing H_2SO_4 to peroxydisulphuric acid in the "Peracidox" process.

4.1.2.6.3 The modified lead chamber process

The Modified Lead Chamber Process is able to treat gases with low SO_2 content (as low as 0.05%) up to 8%. The process is also able to treat gases containing a mixture of SO_2 and NO_x . From the chemical point of view, the process is a development of lead chamber sulphuric acid technology, in which nitrogen oxides are used to promote sulphuric acid production directly from sulphur dioxide through the formation of an intermediate, nitrosyl sulphuric acid. Widely used in the early 1900s, this technology has been largely superseded by the contact process.

After dust removal and purification, the sulphur dioxide-containing gas is fed through a denitrification system, where final traces of nitrogen oxides remaining in the sulphuric acid are removed. It is then passed through the Glover tower where the bulk of the nitrogen oxides are removed from the sulphuric acid. Sulphur dioxide is then absorbed from the gas stream into sulphuric acid (59 to 66%) in a packed tower. In both the Glover and absorption towers, the gas flow is counter current to the liquid flow. The final step of the process is the removal of

nitrogen oxides from the gas stream by absorption in sulphuric acid (74%), forming nitrosyl sulphuric acid. Absorption is achieved in three stages in a specially designed packed vessel through which the gas flows horizontally. This vessel allows multiple absorption without dead space between stages. (This design is also employed for the final removal of nitrogen oxides from sulphuric acid). The absorber has dividing walls that are permeable to the gas between each stage. Packing is placed between the dividing walls.

Regulation of the NO/NO_2 ratio, which is important for the absorption of nitrogen oxides, is achieved by adjusting the amount of nitrosyl sulphuric acid fed to the Glover tower. If necessary the nitrogen oxide balance is maintained by adding nitric acid to the Glover tower. For SO_2 contents of 0.5 to 8%, the conversion efficiency is about 100% but emissions of NO_x occur (up to 1g.Nm^{-3} of $\text{NO} + \text{NO}_2$).

Since 1974, Ciba-Geigy has been developing such a process specifically designed for processing gases with about 0.5-3% volume SO_2 .

4.2 Environmental Performance

The main pollutants emitted are:-

- SO_2 resulting from incomplete oxidation
- SO_3 resulting from incomplete absorption of SO_3
- Droplets of H_2SO_4 resulting from absorption
- H_2SO_4 vapour from scrubbing

Many other pollutants may be emitted in trace amounts depending on the source of SO_2 and the H_2SO_4 production process. For example:-

- NO and NO_2 from all processes but mainly from those such as the Modified Lead Chamber Process, based on NO_x
- Heavy metals (for example, mercury) when certain ores are treated

4.2.1 Monitoring of pollution

Two approaches are used to monitor emissions:-

- Monitoring the process: for example, the temperature of contact beds or the SO_2 content entering the contact section and behind the intermediate absorption
- Monitoring of the emissions

4.2.1.1 Monitoring of SO_2 emissions

Continuous emission monitoring equipment for SO_2 is available and suitable for sulphuric acid plants and should be installed on all plants. Dual range instruments are available so that the much higher SO_2 emission concentration during start-up can be monitored as well as the relatively low concentration in the emission during steady operation. Emission monitor records should be retained and the competent authorities should consider the appropriate statistical analysis or reporting which is required.

See References [4], [7], [10], [11] for the analytical methods for the determination of SO₂ and References [8], [9] for on-line sampling and measuring.

Measurement problem:-

SO₂ concentration; Span 0-1,000 ppm

Matrix: air, H₂O, H₂SO₄ [30ppm], NO_x [50ppm]

Commercially available IR or UV photometers can be used for this range and matrix but IR measurement requires compensation for the water present.

Two kinds of photometer are available:-

- Inline photometers (only IR) are able to measure the gas concentration inside the gas pipeline provided the matrix is transparent for the optics (e.g. no fog)
- Online photometers with sample preparation

The second method is the normal method but suitable materials must be chosen for the sample preparation and the measuring cell because of corrosion.

There are two methods of sample preparation:-

- Hot sample preparation keeping the sample and the whole sampling equipment (filter, pipeline, pump, measuring cell) above the dewpoint (~ 150°C)
- Cold sample preparation using a cooler to dry the sample gas to a fixed dewpoint (~5°C)

Any method of SO₂ measurement needs a certain amount of maintenance for high availability and reliability. Appropriate plans with intervals for inspection and service should be made, including information for maintenance in the case of breakdown. The accuracy of the analysers lies between 1 and 2%. The overall precision of a complete system lies between 2 and 5%. Statutory conditions must be observed for the analyser and sampling system in special circumstances such as environmental protection. Concentration values are registered and stored in an additional system such as PCS or a special datalogger.

Provision should be made for zero and calibration checks of emission monitors, and for alternative testing in the event of breakdown or suspected malfunctioning of the monitoring equipment. The regular observation of monitors by plant operators for detecting abnormalities in the process operation is as important an aspect of monitoring as is the compliance function, and should be encouraged by the competent authorities [32].

4.2.1.2 Monitoring of mist emissions in the stack

There is at present no known equipment available for carrying out reliable continuous monitoring of sulphur trioxide. Meanwhile, sulphur trioxide together with sulphuric acid mist can be measured by manual sampling and chemical analysis [4]. The analytical problem of separation between SO₃/H₂SO₄ and SO₂ is well solved by the method of 'Specht' which uses boiling aqueous hydrogen chloride for absorption of SO₃/H₂SO₄.

Sampling points for the above measurements under iso-kinetic conditions should be provided. They must be easily accessible and kept in good condition so that they can be used at very short notice. Sealable openings 20 to 50mm diameter are generally considered as suitable, provided that a sampling probe can be inserted into the exhaust gas stream, except in cases when standardised methods require the use of larger openings.

4.2.2 General techniques

4.2.2.1 Process control optimisation

Operational controls should include means for:-

- Warning of absorber acid feed failure
- Warning of absorber acid feed over-temperature and controls of temperature along the conversion tower
- Indication of sulphur feed rate and air flow rate
- Detection of acid leaks in acid coolers (pH-meter) and controlling the level of the acid reservoir
- Acid-concentration > 98.5%
- Emergency plant trips
- pH-control on cooling water systems

To aid start-up the following will be necessary:-

- Efficient catalyst preheating facilities, vented to the chimney. At least, two catalyst stages must be above “strike” temperature before sulphur dioxide is admitted to contact the catalyst
- Optimisation of absorber acid strength and temperature before sulphur is admitted to the burner
- Use of additional controls to ensure that sulphur cannot enter the system during shut-down
- Before a long shut-down period the catalyst bed should be efficiently purged of SO_2/SO_3

4.2.2.2 Fuels and raw materials selection

4.2.2.2.1 Sulphur

Sulphur with low contents of ash, water and sulphuric acid must be preferred.

4.2.2.2.2 Energy for heating systems

Heating systems are required for the start-up of sulphuric-acid plants. Where direct combustion is applied, low sulphur fuels are preferable.

4.2.3 Techniques to control emissions of SO₂

Table 10 gives an overview of techniques that have a positive effect on, that is reduce, the emissions of SO₂ during the manufacture of sulphuric acid. Most sulphuric acid plants have taken general primary optimisation measures, like process control measures.

Table 10 Techniques Having a Positive Effect on Emissions of SO₂

Techniques	Applicability in processes	Emission Level referring to 11% SO ₂ and 1,000 t.d ⁻¹ = 100,000 Nm ³ .h ⁻¹		Cost (in addition to the basic installation)		Additional effects
		mg SO ₂ .Nm ⁻³ tail gas	kg SO ₂ .t ⁻¹ H ₂ SO ₄ 100%	Investment	Operating	
Contact process						
Single absorption + 5 th bed	all s.a.	< 5,000	< 10	1 to 3M EUR	0.2 EUR.t ⁻¹	
Double absorption + 5 th bed	all d.a.	< 1,000	< 2.5	1 to 3M EUR	0.2 EUR.t ⁻¹	
Single absorption + caesium catalyst in the last bed	all s.a.	< 4,500	< 9	35k EUR	0	
Double absorption + caesium catalyst in the last bed	all d.a.	< 900	< 2.3	35k EUR	0	
Single to double absorption	s.a.	< 1,000	2.6	6.5M EUR	3.8 EUR.t ⁻¹	
Tail gas scrubbing						
Sodium hydroxide	all	< 200	< 2	6M EUR	4.5 EUR.t ⁻¹	Sodium salt to be disposed of
Ammonium hydroxide	all	< 200	< 2	6M EUR	4.4 EUR.t ⁻¹	Ammonium salt to be disposed of
Calcium hydroxide	all	< 200	< 2	6M EUR	4.0 EUR.t ⁻¹	Gypsum to be disposed of
Activated carbon	all	< 1,000	< 2	5.5M EUR	4.0 EUR.t ⁻¹	Dilute sulphuric acid
Hydrogen peroxide treatment after end absorption	all	< 200	< 2	4.5M EUR	6 EUR.t ⁻¹	Dilute sulphuric acid

4.2.4 Techniques to control emissions of SO₃ and H₂SO₄

Table 11 gives an overview of techniques that have a positive effect on, that is reduce, the emissions of H₂SO₄ (taken as the sum of SO₃ and H₂SO₄) during the manufacture of sulphuric acid. Most sulphuric acid plants have taken general primary optimisation measures, like process control measures.

Table 11 Techniques Having a Positive Effect on Emissions of H₂SO₄

Techniques	Applicability	Emission Level		Additional cost		Additional effects
		mg H ₂ SO ₄ .Nm ⁻³ tail gas	kg.t ⁻¹ H ₂ SO ₄ 100%	Investment	Operating	
Wire-mesh	Large droplets (1μ-20μ)	< 100				Not efficient on mists
High efficiency candle type filter after absorbers	0,1μ to 2μ droplets	< 50	< 0.03	0.5M EUR	30 EUR.y ⁻¹	– increased energy consumption – production loss – capacity loss – plume suppression
Scrubbing	all	< 10	0.015	As in table 10.	As in table 10.	– waste generation as in table 10. – plume reduction

4.3 Economic Performance

The estimated Investment Costs for a 1,000t.d⁻¹ H₂SO₄ sulphuric acid process plant are:-

- Double absorption with 11% SO₂, 4-bed double contact without caesium catalyst: 20 to 30M EUR
- Single absorption with 3-6% SO₂, 4-bed single contact without caesium catalyst: 18 to 25M EUR

Operating cost:-

The economic considerations are based on a sulphuric acid price between 30 and 60 EUR.t⁻¹ H₂SO₄

4.3.1 Additional processes

An additional process will be needed if process optimisations are not sufficient to reach the SO₂ emission administrative limit. The “Best Available Technique” for this will mainly depend on the site or company opportunities.

For example: NH₃ scrubbing could be the BAT on a fertilizer site; Ca(OH)₂ scrubbing could be the BAT if gypsum can be used in the plaster or cement industries and double absorption will be the BAT if no by or co-product can be accepted.

Additional process impacts

Capital costs:-

The following figures can be considered on the basis of a 500t.d⁻¹ H₂SO₄ production facility, corresponding to an SO₂ reduction of 5t.d⁻¹ to the atmosphere:-

Process	Costs
Changing Single to Double Absorption (If the existing converter can be used as it is)	4.5M EUR
H ₂ O ₂ oxidation process	3M EUR
– OH scrubbing processes	4M EUR

These figures may be modified according to each specific facility.

Operating costs:-

Type of costs	Double absorption	H ₂ O ₂	– OH scrubbing
Fixed costs/year			
Personnel	0	1 person	6 persons
Maintenance	135k EUR	90k EUR	120k EUR
Variable costs/year			
Electricity	130k EUR	100k EUR	100k EUR
Raw materials	–60k EUR	540k EUR	120k EUR
Co-product disposal	0	0	–10k EUR
Total costs/year	205k EUR	730k EUR	330k EUR

SO₂ reduction leads to a cost of 110 to 440 EUR for each tonne of SO₂ abated, excluding depreciation.

In conclusion, double absorption is a suitable way of reduction when:-

- The plant configuration (mainly the converter) and space allows the transformation
- There is no valuable use of any by-product

Depending on the process selected, the SO₂ reduction leads to an additional cost per tonne of H₂SO₄ produced, including depreciation over 10 years, of:-

- | | |
|---|--|
| – Double absorption | 3.8 EUR |
| – H ₂ O ₂ abatement | 6 EUR |
| – OH abatement (as NH ₃) | 4.4 EUR (for a selling price of the by-product at 0 EUR) |

Hypothesis: Estimated price for: Electricity: 38 EUR.MWh⁻¹
H₂O₂: 610 EUR.t⁻¹ (100%)
– OH as NH₃: 122 EUR.t⁻¹

5. BEST AVAILABLE TECHNIQUES

Article 2.11 in Council Directive 96/61/EC concerning integrated pollution prevention and control says: ‘best available techniques’ shall mean the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing, in principle, the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as whole.

Candidate best available techniques are identified and described in Chapter 4. The selection of BAT is made in this Section, based on the information given in Chapter 4 and considering achievable emission levels, the applicability and the cost of the techniques. The present Booklet does not deal in detail with the storage and handling of raw materials (sulphur, pyrites, ore, spent acid, sulphates, etc.) used to produce SO_2 .

Chapter 4 has presented the different sources of SO_2 and the techniques of conversion of SO_2 to SO_3 best adapted to each kind of source. These techniques of conversion have their own typical conversion rate and consequently their SO_2 emission concentration expressed in $\text{kg SO}_2 \cdot \text{t}^{-1} \text{H}_2\text{SO}_4$ or $\text{mg SO}_2 \cdot \text{Nm}^{-3}$ or $\text{ppm SO}_2/\text{H}_2\text{SO}_4$ (measurements of concentration and flow rate).

The process conditions and the SO_2 concentration in the gas entering the converter determine the conversion efficiency which directly influences the SO_2 emission concentration (see Figure 2). The SO_3 and H_2SO_4 content in the tail gases depend on the raw material and the process. The content of gaseous SO_3 and H_2SO_4 mist in the tail gases is essentially a function of the temperature and concentration of the irrigation acid in the final absorber.

The following BATs are presented for new plants due to the fact that it is generally not possible to change the source of SO_2 or to change or modify the conversion process. For existing plants, only tail gas scrubbing can be generally considered as a BAT taking into account that the addition of tail gas scrubbing to a double absorption plant is considered as entailing excessive costs (see 4.3) and could be justified only by severe local considerations.

5.1 BAT for the Different Types of Sulphuric Acid Processes

5.1.1 Sulphur burning

Due to the high concentration of SO_2 and stability over time, the BAT is without doubt the **double contact** process. There are two alternatives to achieve the highest possible conversion efficiency in this process.

- Select a caesium-promoted catalyst with a lower working temperature in one or several layers, usually in the last layer. Four layers are normally sufficient. A caesium-promoted catalyst is about three times more expensive than the usual catalyst
- Increase the catalyst volume with a cheaper normal catalyst in four layers. The better method is to add a fifth layer

In both alternatives a conversion efficiency of 99.6% (daily average except start-up and shut-down conditions) can be achieved in new plants.

5.1.2 Metal sulphide roasting/smeltering

5.1.2.1 Pyrites roasting

Although the stability over time is slightly variable, the BAT should be the double contact process with a conversion efficiency of about 99.5 to 99.6% depending on the quality of the pyrites (daily average excluding start-up and shut-down conditions): The same two options are available to achieve the highest possible conversion efficiency as for sulphur burning (see 5.1.1).

5.1.2.2 Zinc roasting

As the range of SO_2 content after possible dilution is about 6 to 13% and the variability over time is low, the double contact process can be used as BAT with a conversion efficiency of about 99.6% (daily average except start-up and shut-down conditions) when using gases with SO_2 content $>8\%$.

5.1.2.3 Copper smelting

When the SO_2 content in gases is high (6-13% after possible dilution) and the variability over time is low, the double contact process can be considered as BAT with a conversion efficiency of about 99.6% (daily average except start-up and shut-down conditions).

When the SO_2 content in gases is low (1-6%) and the variability over time is high, the single contact process can be considered as BAT with a conversion efficiency of about 98.5% (daily average except start-up and shut-down conditions).

When the SO_2 content is 5-10% and the variability over time is high, the double contact process can be considered as BAT with a conversion efficiency of about 99.5% (daily average except start-up and shut-down conditions).

When a plant experiences the full range of variability, the efficiency will vary between 98 and 99.5%. Similar circumstances will permit an achievable SO_2 level, in terms of converter throughput based on 100% H_2SO_4 acid of between 3-6kg $\text{SO}_2 \cdot \text{t}^{-1}$ H_2SO_4 due to fluctuating absorption conditions.

The key to a correct purification of metallurgical gases lies in continuous, stable operation of the purification process, normally in an acid plant. The gas flows, which are susceptible to wide fluctuations in volume and concentration, are to some degree incompatible with this criterion. Fluctuations can be minimised by carrying out the conversion process in various converters, or by mixing the gases with the more concentrated flow coming from the smelting stage. This produces gas flows with a concentration range that is adequate to maintain the autothermal process. This is the procedure followed in modern copper smelters that use Outokumpu flash smelting furnaces and Pierce Smith converters.

5.1.2.4 Lead smelting

In the case of sintering lead ores, the variability is relatively high and SO₂ content can be very low, the single contact process and also the wet process and the process based on NO_x can be considered as BAT with conversion efficiencies of about 98.5, 98 and 100% respectively. This low or variable SO₂ content is due to a down-draught sintering which limits SO₂ emissions. In other cases (lead smelters), the SO₂ can be much higher and less variable over time. In this case the double contact process can be considered as BAT with a conversion efficiency of about 99.5% (daily average except start-up and shut-down conditions).

It has not been possible to arrive at precise limits for the chosen BAT. Apart from costs, conversions and theoretical considerations and also local regulations need to be taken into account to decide the right BAT. The Technical Note on BAT for heavy metal production covers this point and it is recommended that this document should be consulted on this issue.

5.1.3 Sulphuric acid regeneration

The O₂/SO₂ ratio is important to achieve as high a conversion rate of SO₂ to SO₃ as possible. The gases are reheated to the ignition temperature through gas/gas heat exchangers using the heat of conversion, upstream of the converter. A double absorption process can only be used if the SO₂ content of the gases is high enough (about 8%) at the converter inlet. The conversion rates for different SO₂-concentrations are shown below:-

Single absorption

SO ₂ content at the converter inlet	8%	with O ₂ /SO ₂ ratio of	1.1: 98%
SO ₂ content at the converter inlet	from 5 to 8%	with O ₂ /SO ₂ ratio of	1.1: 97 to 98%
SO ₂ content at the converter inlet	below 5%	with O ₂ /SO ₂ ratio of	1.1: 96 to 97%

Double absorption

When achievable, leads to conversion rates from **99 to 99.6%**

Double absorption is considered as BAT for new plants. For existing plants, a single absorption can be advantageously combined with an ammonia scrubber, the by-product obtained being either sold on the market or recycled in the furnace.

5.1.4 Metal sulphate roasting

The conclusions are the same as those for sulphuric acid regeneration.

5.1.5 Combustion of H₂S and other S-containing gases

The conclusions are the same as those for sulphuric acid regeneration.

5.2 BAT for Contact Processes

5.2.1 In respect of SO₂ emissions

Table 12 BAT Limits for SO₂ Emissions Dependent on Process Type and Absorption Type

process type for manufacturing sulphuric acid	range for SO ₂ conc.	single absorption	double absorption *	double absorption + Bed 5 or Bed 4 caesium *	single absorption + tail gas scrubbing with usage byprod.
	Vol. % SO ₂	kg SO ₂ .t ⁻¹ H ₂ SO ₄	kg SO ₂ .t ⁻¹ H ₂ SO ₄	kg SO ₂ .t ⁻¹ H ₂ SO ₄	kg SO ₂ .t ⁻¹ H ₂ SO ₄
sulphur burning	6-12	6.7-13.3	1.5-3.9	1.0-2.6	<2
pyrites roasting	8-10		2.6-3.9	1.5-3	<2
zinc/lead ores roasting	4-9	7-12 (4-6% SO ₂)	1.7-3.3 (6-12% SO ₂)	1.5-2.5	<2
copper smelting	3-13	6.5-20	1.2-3.3	1.2-2.5	<2
lead/copper smelting	2.7	6-10			< 2
organic spent acid regeneration	2-10	10-27	2.6-6.6	1.5-4.5	<2
metal sulphate roasting	8-12		1.6-3.3	1.3-2.6	-

* Not achievable for low SO₂ gas content

5.2.2 In respect of H₂SO₄ emissions

Table 13 BAT Limits for H₂SO₄ Emissions Dependent on Process Type and Absorption Type

process type for manufacturing sulphuric acid	range for SO ₂ conc.	single absorption	double absorption	double absorption + Bed 5 or Bed 4 caesium	single absorption + tail gas scrubbing with usage byprod.
	Vol. % SO ₂	kg H ₂ SO ₄ *.t ⁻¹ H ₂ SO ₄	kg H ₂ SO ₄ *.t ⁻¹ H ₂ SO ₄	kg H ₂ SO ₄ *.t ⁻¹ H ₂ SO ₄	kg H ₂ SO ₄ *.t ⁻¹ H ₂ SO ₄
sulphur burning	6-12	< 0.1	< 0.1	< 0.1	< 0.1
pyrites roasting	8-10	0.2	0.2		
zinc/lead ores roasting	4-9	0.15-0.3 (4-6% SO ₂)	0.1-0.16 (6-12% SO ₂)		
copper smelting	3-13	0.06-0.35	0.05-0.2		
lead/copper smelting	2.7	0.15			
organic spent acid regeneration	2-10	0.05-0.2	0.05-0.2		0.01-0.03
metal sulphate roasting	8-12		0.065-0.13	0.065-0.13	

* H₂SO₄ = SO₃ + H₂SO₄

5.2.3 In respect of energy output

Table 14 BAT Limits for Energy Outputs Dependent on Process Type and Absorption Type [16]

process type for manufacturing sulphuric acid	range for SO ₂ conc.	single absorption	double absorption
	Vol. % SO ₂	MJ.t ⁻¹ H ₂ SO ₄	MJ.t ⁻¹ H ₂ SO ₄
sulphur burning	6-12		2,500
pyrites roasting	8-10		4,500
zinc/lead ores roasting	4-9		600
		(4-6% SO ₂)	(6-12% SO ₂)
copper smelting	3-13	2,000-2,900	2,000-2,900
lead/copper smelting	2.7	900	
organic spent acid regeneration	2-10	2,500	2,500

5.2.4 The role of scrubbing and tail gas processes

Tail gas scrubbing produces sulphites and sulphates which may give rise to waste disposal problems. However, they are applicable if sodium bisulphite, ammonium sulphate or gypsum are produced as marketable by- products near the sulphuric acid plant.

5.2.5 Energy consideration on plants with double and single absorption

Energy has been considered for different SO₂ concentrations, 5% and 11% Vol, and for single/double absorption processes. The starting inlet gas is dry SO₂ gas at 20°C. The end product is sulphuric acid at 98.0% and 25°C. The energy (+ supply, – removal) values are given as MJ.t⁻¹ 100% H₂SO₄.

The temperature point in the region of 180°C is the gas dewpoint. In newer techniques energy is recoverable up to 120°C. Five cases are evaluated:-

- 11% SO₂ Double contact (3 + 2)
- 11% SO₂ Double contact (2 + 2 + heat recovery system)
- 11% SO₂ Double contact (2 + 2)
- 5% SO₂ Double contact (2 + 2)
- 5% SO₂ Single contact (4 beds)

Table 15 Energy Considerations on Plants with Double Absorption

	theoret. conv.%	MJ.t ⁻¹ H ₂ SO ₄	Energy status	Energy Level
11% SO₂ Double contact (3+2)				
Gas inlet 80°C → 430°C		972	recovering	Heat exchanger
bed 1 430°C → 582 → 430°C	48.80	-462	recovering	Heat exchanger
bed 2 430°C → 520 → 430°C	77.60	-273	recovering	Heat exchanger
bed 3 430°C → 478°C → 180°C	92.84	-871	recovering	Heat exchanger
Interabsorption 180°C → 80°C		-1,353	lost	Cooling with water/air
after interabsorption 80°C → 430°C		799	recovering	Heat exchanger
bed 4 430°C → 457 → 430°C	99.61	-64	recovering	Heat exchanger
bed 5 430°C → 431°C → 180°C	99.78	-578	recovering	Heat exchanger
end absorption 180°C → 80°C		-443	lost	Cooling with water/air
Sulphuric acid 25°C 98%		-97	lost	Cooling with water
		-477	recovering	
		-1,893	lost	Cooling with water

11% SO₂ Double contact (2+2 + Heat recovery system)

Gas inlet 80°C → 430°C		972	recovering	Heat exchanger
bed 1 430°C → 582°C → 430°C	48.80	-462	recovering	Heat exchanger
bed 2 430°C → 520°C → 180°C	77.60	-998	recovering	Heat exchanger
Interabsorption 180°C		-659	recovering	Heat exchanger
after interabsorption 180°C → 430°C		598	recovering	Heat exchanger
bed 3 430°C → 457°C → 430°C	99.61	-192	recovering	Heat exchanger
bed 4 430°C → 436°C → 180°C	99.78	-617	recovering	Heat exchanger
end absorption 180°C → 80°C		-883	lost	Cooling with water/air
outlet sulphuric acid 25°C/98%		-112	lost	Cooling with water
		-1,357	recovering	
		-995	lost	Cooling with water

11% SO₂ Double contact (2 + 2)

Gas inlet 80°C → 430°C		972	recovering	Heat exchanger
bed 1 430°C → 582°C → 430°C	48.80	-462	recovering	Heat exchanger
bed 2 430°C → 520°C → 180°C	77.60	-998	recovering	Heat exchanger
Interabsorption 180°C → 80°C		-1,167	loss	Cooling water/air
after interabsorption 80°C → 430°C		830	recovering	Heat exchanger
bed 3 430°C → 457°C → 430°C	99.61	-192	recovering	Heat exchanger
bed 4 430°C → 436°C → 180°C	99.78	-617	recovering	Heat exchanger
end absorption 180°C → 80°C		-623	lost	Cooling with water/air
outlet sulphuric acid 25°C/98%		-103	lost	Cooling with water
		-465	recovering	
		-1,893	lost	Cooling with water

theoret. conv. %	MJ.t ⁻¹ H ₂ SO ₄	Energy status	Energy Level
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5% SO₂ Double contact (2 + 2)

Gas inlet 80°C → 430°C		946	recovering	Heat exchanger
bed 1 430°C → 538°C → 430°C	72.91	-315	recovering	Heat exchanger
bed 2 430°C → 461°C → 180°C	93.52	-789	recovering	Heat exchanger
Interabsorption 180°C → 80°C		-718	loss	Cooling water/air
after interabsorption 80°C → 430°C		875	recovering	Heat exchanger
bed 3 430°C → 441°C → 430°C	99.85	-27	recovering	Heat exchanger
bed 4 430°C → 430°C → 180°C	99.88	-631	recovering	Heat exchanger
end absorption 180°C → 80°C		-347	lost	Cooling with water/air
outlet sulphuric acid 25°C/98%		-43	lost	Cooling with water
		60	recovering	
		-1,108	lost	Cooling with water

5% SO₂ Single contact (4 bed)

Gas inlet 80°C → 430°C		946	recovering	Heat exchanger
bed 1 430°C → 538°C → 430°C	72.91	-315	recovering	Heat exchanger
bed 2 430°C → 461°C → 430°C	93.52	-89	recovering	Heat exchanger
bed 3 430°C → 437°C → 430°C	98.24	-20	recovering	Heat exchanger
bed 4 430°C → 431°C → 180°C	98.88	-703	recovering	Heat exchanger
end absorption 180°C → 80°C		-347	lost	Cooling with water/air
outlet sulphuric acid 25°C/98%		-43	lost	Cooling with water
		-180	recovering	
		-390	lost	Cooling with water

5.2.6 Effect of the emission/consumption level

The production and consumption of sulphuric acid is influenced by:-

- The cost of sulphuric acid
- The cost of transport
- The quality of the different acids relative to the use
- Safety during transport and storage and emissions
- The environmental regulation at the production site
- The future development of regeneration of spent acids

A flowsheet for sulphuric acid production, consumption and use indicates the different influences:-

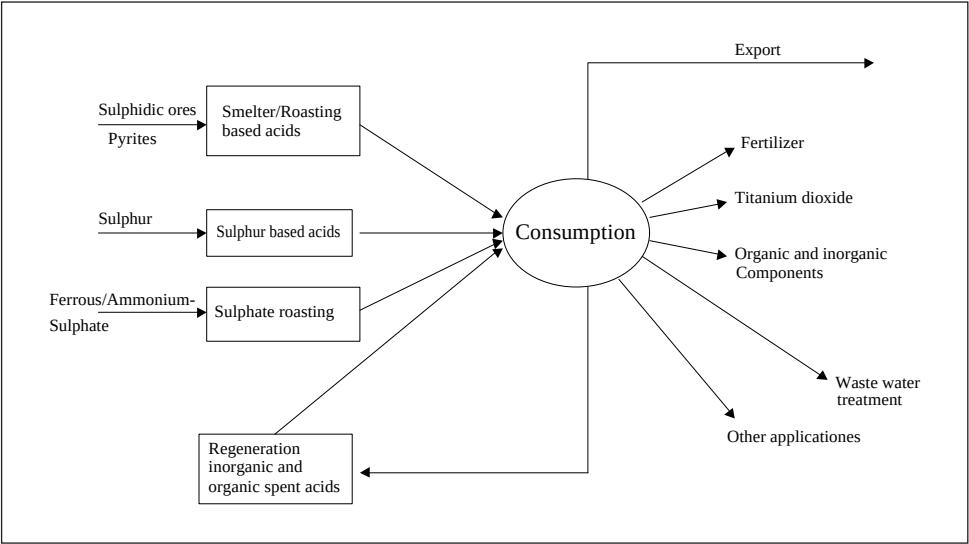


Figure 7 – Flowsheet for Sulphuric Acid Production.

5.3 Cross Media Impact

The minimisation of SO₂ emissions to the atmosphere can lead to different impacts, depending on the route of reduction. The metal sulphide sector will emphase that sulphuric acid production is not the prime objective of the process, which remains the production of non-ferrous metal. Sulphuric acid production arises from the necessity to reduce the SO₂ emission.

5.3.1 Tail gas scrubbing

Tail gas scrubbing transfers the SO₂ from tail gases to a by-product which can be in solution or solid. Disposal of this by-product on the soil or into water (sea/river) can be considered as a pollution transfer and thus this kind of technique must be associated with recycling or use of the by-product on site or on a customer site over a certain period of time.

5.3.2 Caesium catalyst

The use of large amounts of caesium catalyst will have an impact on caesium production and disposal of the spent catalyst.

5.3.3 Electricity

Practically all the processes for SO_2 reduction lead to an increase in electricity consumption, mainly due to the pressure drop increase. This point impacts on the need for electricity generation and can have some consequences for CO_2 , SO_2 and dust emissions from electricity power stations.

5.3.4 Cooling water effect to the atmosphere

On a sulphuric acid plant the majority of the conversion energy is recovered as steam, but the absorption energy must be removed either totally or partially and this is generally achieved by water cooling. The cooling water system can be once through when large amounts of water are available, or may use an atmospheric cooling tower. In both cases, the recovered energy is transformed to water evaporation to the atmosphere.

6. EMERGING TECHNIQUES

Sulphuric acid had been produced for many years and has the highest world production of any chemical. Most of the developments in production techniques have been made in the last 100 years and there is little scope for improvement. Sulphuric acid production is a mature industry and hence there is little room for further improvement in the process itself. There have been some developments in the materials used in the construction of the plants or their design such as the use of double shell vessels. These are mainly designed to reduce accidental pollution. Other developments have taken place in the following fields:-

- Energy recovery from primary energy
- Product quality with respect to the content of NO_x and SO_2 which can give rise to emission problems for the customer. NO_x has to be destroyed and any SO_2 stripped with air
- Demisters with very high efficiency

Currently the need is to optimise sections in the different process stages depending on site requirements and local conditions.

7. CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

Two different groups of sulphuric acid production plants can be considered:-

- Plants built before 1970
- Plants built after 1970

The first group were designed on the basis of a single absorption process, with associated conversion rates in the range of 96 to 98.5%. The second group operate the double absorption process, with conversion rates in the range of 99 to 99.7%. It has been noticed that large differences exist between these two groups, mainly depending on the upstream process generating the SO₂ – containing gases.

Some processes (sulphur burning for example) generate SO₂ – rich and non variable gases leading to the highest conversion rates. Some others (spent acid regeneration for example) generate SO₂-lean and/or variable gases with corresponding lower conversion rates. In certain cases it is impossible to use a double absorption process. The conversion efficiency for the metallurgical plants depends on the fluctuations of the SO₂ concentration at the inlet to the plant.

The situation in Western Europe since 1990 is shown in Tables 16 and 17.

Table 16 Project List of “New” Plants in Western Europe

Location	Company	Capacity	Year of start up	Ref.
Aviles, Spain	Asturiana de Zinc S.A.	n.a	1998	[31]
Sweden	Boliden	910t.d ⁻¹	2000	
Porto Maghera, Italy	Enichem	540t.d ⁻¹	n.a.	
Sardinia, Italy	Sarlux	339t.d ⁻¹	n.a.	
Budel	Budelco	1,185t.d ⁻¹	n.a.	

Innovative techniques with environmental performance better than the listed techniques are not possible:-

- A zero emission level is effectively achieved with a conversion rate above 99.9%
- Maximum recovery of energy is technically possible

Sulphuric acid is one of the oldest industrial chemicals. A large number of improvements concerning emissions and energy recovery have been made by the industry over a long period of time. Today all sulphuric acid industries in Western Europe have taken the big responsibility to cut sulphur emissions down to a very low level. In order to improve the environment it is better to invest money to prevent the “Greenhouse” effect for example. There is no carbon dioxide emission when producing energy from sulphur.

Table 17 List of Plants Built after 1990 in Western Europe

Location	Process type	Costs	Company	Capacity t H ₂ SO ₄ .d ⁻¹	Year of start up	Emission level	Ref.
			Rhone-Poulenc				*)
Hamburg, Germany	Cu Smelter acid (5-8.4% SO ₂) 5. bed	1M EUR	Norddeutsche Affinerie	918t.d ⁻¹	1991	< 800mg SO ₂ .Nm ⁻³	[25]
Helsingborg, Sweden	Sulphur burning 17.5% SO ₂ H ₂ O ₂ scrubbing tower, 5. bed	36M EUR	Kemira Kemi	1,000t.d ⁻¹	1992	< 0.9kg SO ₂ .t ⁻¹ H ₂ SO ₄	[26]
Hartjavalta, Finland	Copper and nickel based smelter acid 7-12% SO ₂	33M EUR	Outokumpu extension	2,430t.d ⁻¹	1995	< 4,500t SO ₂ .y ⁻¹	[27]
Tessenderlo, Belgium	Sulphur burner, 11.5% SO ₂ , heat recovery system		Tessenderlo Chemie	1,000t.d ⁻¹	1992	300ppm SO ₂	[28]
Leuna, Germany	Sulphur burner 5. bed		Domo		1996	99.9% conversion rate	[29]
Huelva, Spain	Cu Smelter acid (5-10.2% SO ₂)	39M EUR	Atlantic Copper	1,270t.d ⁻¹	1996	>99.6%	
Ludwigshafen, Germany	Sulphur burner,		BASF	900t.d ⁻¹		0.65kg SO ₂ .t ⁻¹ H ₂ SO ₄	
Le Havre, France	Sulphur burner, double absorption 11.5% SO ₂		Millennium	800t.d ⁻¹	1992	2.6kg SO ₂ .t ⁻¹ H ₂ SO ₄	
Huelva, Spain			Fertiberia	2,400t.d ⁻¹	2000		
Worms, Germany	Spent acid regeneration; H ₂ SO ₄ (NH ₄) ₂ SO ₄	53M EUR	Rhöm GmbH	500t.d ⁻¹	1994		[30]

***) Practice from a large producer:** For the Rhone-Poulenc group in Europe, during the last 10 years; 5 plants representing a production capacity about 3,600t.d⁻¹ have been transformed or are going to be transformed to achieve the equivalent of Double Absorption process: 2 of them from SA to DA, 3 of them with additional SO₂ abatement.

All new plants with stable and high sulphur dioxide concentrations ($> 6\%$), are built using the double contact process and to high energy standards. Most of the old plants have been improved to a good conversion rate and a high energy standard.

Based on these facts the conclusion is that for gases with 6-12% SO_2 a double absorption process with an average conversion rate of at least 99.6% is achievable. On the other hand for poor gases or fluctuating gases where a double absorption process is not feasible for practical and theoretical reasons, a single absorption process can be considered as BAT. In this case and with optimal design, a conversion rate of 99% can be achieved.

7.2 Recommendations

On the basis of 7.1, the following recommendations are made:-

1. For new plants, the Double Absorption process has to be considered as the BAT, when achievable. The average conversion rate corresponding to this technique is at least 99.6% for non variable and rich gases ($> 6\% \text{SO}_2$). It is possible to improve this conversion rate by 0.2% by using a caesium catalyst. However, this quite new catalyst is very expensive (3 to 4 times the normal one) and should only be used when local constraints are very severe.
2. For plants operating on a Single Absorption process, different ways can be considered:-
 - Caesium catalyst in the last bed (conversion at least 99%)
 - Transforming Single to Double Absorption process
 - SO_2 abatement by scrubbing with a neutralising compound
 - SO_2 abatement with hydrogen peroxide H_2O_2

and the BAT will depend on:-

- Site location and opportunities
- Technical possibilities
- Environmental considerations
- Economic criteria

When achievable on a technical basis, a transformation to Double Absorption process can be considered as the BAT. When transformation from Single to Double Absorption is not possible or when there is the possibility of enhanced value for the by-product resulting from the scrubbing (ammonium, sodium, magnesium or calcium salts or solutions), this can be considered as the BAT for old and new plants.

Tail gas scrubbing can be a solution to limit emissions, depending on local legislation, environmental considerations and economic data. In this case, the possible enhanced value for by-products has also to be taken into account and therefore in specific cases only, single absorption can be considered as the BAT.

For tail gas processes with lower sulphur dioxide content or fluctuating concentration it is always a matter of process and each case must be decided for each plant. Depending on the local conditions the recommendation is tail gas treatment with ammonia, calcium hydroxide or sodium hydroxide as described. This level is normally reached by double contact and double absorption but this must always be decided at the plant and, depending on that, all sites have different possibilities due to local conditions.

3. For plants where double absorption is not achievable because of the gas quality and where there is no possible use for a neutralisation by-product, processes able to operate on very poor gases have to be considered as the BAT, with the condition of recycling the by-product (usually sulphuric acid more or less diluted) in the plant. These processes can be:-

- Abatement by scrubbing with H_2O_2
- Activated carbon process

In conclusion to SO_2 emissions minimisation from sulphuric acid plants, for old and new plants the recommendation for the BAT is to take into account:-

- Site opportunities
- The process generating SO_2

Progress made during the last years in the design of absorption towers, and high efficiency demisting systems for SO_3 and H_2SO_4 mists emissions, allow these emissions to be kept to very low levels, as low as 50mg.Nm^{-3} and this could be the BAT.

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GLOSSARY AND UNITS

Glossary

ADR	Accord européen relatif au transport international des marchandises Dangereuses par Route
RID	Règlement concernant le transport International ferroviaire des marchandises Dangereuses
DA	Double absorption
ESP	Electro static precipitator
EUR	Euro
IMO	International Maritime Organisation
IR	Infrared
ISF	Imperial Smelting Furnace (blast furnace for Zn-Pb concentrates)
k EUR	Thousand of Euro
M EUR	Million of Euro
PCS	Process control system
SA	Single absorption
UV	Ultraviolet
WCP	Wet contact process

Units

MWh	Megawatt hour
ppm	Part per million
ppmv	Part per million by volume

APPENDIX Inputs and Outputs

A1 Sulphur Burning Plants with Single Absorption

Inputs		Amount	Unit	Comments
	SO ₂	6-12	%	degree of variability: Low
	O ₂	9-15	%	degree of variability: Low
	CO ₂	0	%	degree of variability: No
	Water (in the gas)	10	mg.Nm ⁻³	
Outputs	Energy	2,500	MJ	net balance
	Emissions into air			
	SO ₂ *	6.7-13.3	kg.t ⁻¹ ***	
	SO ₃ *	0.03	kg.t ⁻¹ ***	
	H ₂ SO ₄ *	0.03	kg.t ⁻¹ ***	
	NO _x **	< 30	mg.Nm ⁻³	
	CO ₂	0	%(vol)	
	Emissions into water	0		no emission into water
	Solid emissions	10	g.t ⁻¹	spent catalyst
	Conversion rate	98-99	%	
	Emission with the final product			
	As	< 0.01	ppm	
	Hg	< 0.01	ppm	
	Se	< 0.01	ppm	
	F	< 0.01	ppm	
	SO ₂	< 30	ppm	
	NO _x	< 30	ppm	
	HCl	< 1	ppm	
	organic carbon	< 1	ppm	

*: expressed as SO₂

**: expressed as NO₂

***: in kg.t⁻¹ 100% sulphuric acid

A2 Sulphur Burning Plants with Double Absorption

Inputs		Amount	Unit	Comments
	SO ₂	6-12	%	degree of variability: Low
	O ₂	9-15	%	degree of variability: Low
	CO ₂	0	%	degree of variability: No
	Water (in the gas)	10	mg.Nm ⁻³	
Outputs	Energy	2,500	MJ	net balance
	Emissions into air			
	SO ₂ *	1.5-3.9	kg.t ⁻¹ *****	
	SO ₃ **	0.1	kg.t ⁻¹ *****	
	H ₂ SO ₄ **	0.1	kg.t ⁻¹ *****	
	NO _x ***	< 30	mg.Nm ⁻³	
	CO ₂	0	%(vol)	
	Emissions into water	0		no emission into water
	Solid emissions	10	g.t ⁻¹	spent catalyst
	Conversion rate	99.2-99.6	%	
	Emission with the final product*****			
	As	< 0.01	ppm	
	Hg	< 0.01	ppm	
	Se	< 0.01	ppm	
	F	< 0.01	ppm	
	SO ₂	< 30	ppm	
	NO _x	< 30	ppm	
	HCl	< 1	ppm	
	organic carbon	< 1	ppm	

* : expressed as SO₂

** : expressed as H₂SO₂

*** : expressed as NO₂

***** : in kg.t⁻¹ 100% sulphuric acid

***** : those values may not be met with certain raw material

A3 Pyrites Roasting

Inputs		Amount	Unit	Comments
	SO ₂	8-10	%	slightly variable over time
	O ₂	8-11	%	
	CO ₂	0	%	
	H ₂ O	0	%	
Outputs	Energy	~4,500	MJ.t ⁻¹ ***	net balance incl. roasting process
	Emissions into air			
	SO ₂ *	3.0	kg.t ⁻¹ ****	
	SO ₃ *	0.2	kg.t ⁻¹ ****	
	H ₂ SO ₄ *	n.a.	kg.t ⁻¹ ****	
	NO _x **	~210	mg.Nm ⁻³	
	CO ₂	0	%(vol)	
	Emissions into water			no emission into water
	Solid emissions	~40	g.t ⁻¹ ****	spent catalyst
	Conversion rate	99.4-99.6	%	
	Emission with the final product			dependent of the analyses of the pyrites The figures are examples from one specific pyrite, see 2.1.2.1.
	As	0.01	ppm	
	Hg	0.03	ppm	
	Se	0.05	ppm	
	F	n.a.	ppm	
	SO ₂	13	ppm	
	NO _x	n.a.	ppm	
	HCl	n.a.	ppm	
	Organic carbon	0	ppm	

* : expressed as SO₂

** : expressed as NO₂

*** : in kg.t⁻¹ 100% sulphuric acid

A4 Zn, Pb Smelter Sulphuric Acid Plants

Inputs		single Abs.		double Abs.	
	% SO ₂	4 ~ 6		5 ~ 9	
	% O ₂	6 ~ 12		6 ~ 11	
	% CO ₂	x		x	
	% H ₂ O	x		x	
	variability in time	low		low	
	Energy MJ.t ⁻¹ .H ₂ SO ₄			~ 600	
Outputs	Air emission at stack	kg.t ⁻¹ H ₂ SO ₄	mg.NO _x .Nm ⁻³	kg.t ⁻¹ H ₂ SO ₄	mg.NO _x .Nm ⁻³
	SO ₂	7 ~ 12	x	1.7 ~ 3.3	x
	SO ₃	0.1 ~ 0.2	x	0.05 ~ 0.08	x
	NO _x		150		150
	H ₂ SO ₄	0.05 ~ 0.1	x	0.05 ~ 0.08	x
	Conversion SO ₂ /SO ₃	98 ~ 99%		99.5 ~ 99.7%	
	H ₂ O emission	no contaminants		no contaminants	
	Spent Catalyst	20 ~ 40g.t ⁻¹ .H ₂ SO ₄ to recycle in process		20 ~ 40g.t ⁻¹ .H ₂ SO ₄ to recycle in process	
	H ₂ SO ₄				
	Hg	max 1ppm			
	As	max 0.5ppm			
	Se	max 0.2ppm			
SO ₂	< 50ppm				
NO ₂	5~30ppm				
Org C	max 1ppm				
Energy steam in Roasting Process MJ.t ⁻¹ .H ₂ SO ₄	3,500				
(waste) heat in acid production:- MJ.t ⁻¹ .H ₂ SO ₄	1,000 ~ 2,000				
Net Balance (In-Out)	3,900 ~ 4,900				

A5 Complex (Pb, Cu) S Batch Treatment

Inputs		single Abs.		double Abs.	
	% SO ₂ % O ₂ % CO ₂ % H ₂ O variability in time Energy MJ.t ⁻¹ .H ₂ SO ₄	2.70% on dry 2.50% on dry 20.00% on dry 45% extremely 900			
Outputs	Air emission at stack	kg.t ⁻¹ H ₂ SO ₄	mg.NO ₂ .Nm ⁻³	kg.t ⁻¹ H ₂ SO ₄	mg.NO ₂ .Nm ⁻³
	SO ₂	6 ~ 10	100		x
	SO ₃	see H ₂ SO ₄			x
	NO ₂				
	H ₂ SO ₄	0.15			x
	Conversion SO ₂ /SO ₃	99.0-99.2%			
	H ₂ O emission	none			
	Spent Catalyst	20 ~ 40 g.t ⁻¹ .H ₂ SO ₄			
	H ₂ SO ₄				
	Hg	<1ppm			
As	<0.2ppm				
Se	<0.5ppm				
SO ₂	90ppm				
NO ₂	150ppm				
Org C	40ppm				
Energy steam in Roasting Process MJ.t ⁻¹ .H ₂ SO ₄	depending on S-content				
(waste) heat in acid production:- MJ.t ⁻¹ .H ₂ SO ₄	1,000 ~ 2,000				
Net Balance (In-Out)	~1,000-2,000				

A6 Copper Smelter Sulphuric Acid Plant

Inputs		Unit	Double Absorption	Single Absorption	Comments
	SO ₂	%	5-13	3-10	degree of variability: High
	O ₂	%	8-16	11-18	degree of variability: High
	CO ₂	%	0-3	0-3	degree of variability: High
	Water (in the gas)	% (vol)	5-7	5-7	
	Process water	m ³ .t ⁻¹	0-0.2	0-0.2	
Outputs	Energy	MJ	2,000-2,900	2,000-2,900	net balance
	Emissions into air				
	SO ₂ *	kg.t ⁻¹ ***	1.2-3.3	6.5-20	
	SO ₃ * + H ₂ SO ₄ *	kg.t ⁻¹ ***	0.05-0.2	0.06-0.35	
	H ₂ SO ₄ *	kg.t ⁻¹ ***			
	NO _x **	mg.Nm ⁻³			Variability: High, depending on smelter O ₂ enrichment
	CO ₂	%(vol)	0-4	0-4	
	Emissions into water				no emission into water
	Solid emissions spent catalyst	g.t ⁻¹	20-40	20-40	5-10% of the installed catalyst and per screening operation
	Conversion rate	%	99.5-99.8	97-99	
	Emission with the final product				
	As	ppm	< 1	Similar to double absorption	
	Hg	ppm	< 1	"	
	Se	ppm	<0.5	"	
	F	ppm	0-2	"	
	SO ₂	ppm	<30	"	
	NO _x	ppm	<40	"	Variability: High, depending on smelter O ₂ enrichment
	HCl	ppm	<5	"	
	organic carbon	ppm	traces	"	Influenced by the smelter fuel combustion burner type (<50)

* : expressed as SO₂

** : expressed as NO₂

*** : in kg.t⁻¹ 100% sulphuric acid

A7 Spent Acid Regeneration

Inputs		Amount	Unit	Comments
	SO ₂	7	%	degree of variability: 2 -10%
	O ₂	8	%	degree of variability: 5-15%
	CO ₂	5	%	degree of variability: 1-10%
	Water (in the gas)	10	mg.Nm ⁻³	
Outputs	Energy	2,500	MJ	net balance
	Emissions into air			
	SO ₂ *	2.6 to 2.7	kg.t ⁻¹ *** DA: 2.6 to 6.6 SA: 10 to 27	
	SO ₃ *	0.03	kg.t ⁻¹ ***	
	H ₂ SO ₄ *	0.03	kg.t ⁻¹ ***	
	NO _x **	0 to 50	mg.Nm ⁻³	
	CO ₂	4	%(vol)	
	Emissions into water	0		no emission into water
	Solid emissions	0	g.t ⁻¹	spent catalyst
	Conversion rate	96 to 99.6	% DA: 99 to 99.5 SA: 96 to 98.5	
	Emission with the final product			
	As	< 0.01	ppm	Depends on the spent acid type
	Hg	< 0.01	ppm	
	Se	< 0.01	ppm	
	F	< 0.01	ppm	
	SO ₂	< 30	ppm	
	NO _x	< 30	ppm	
	HCl	< 1	ppm	
	organic carbon	< 1	ppm	

* : expressed as SO₂

** : expressed as NO₂

*** : in kg.t⁻¹ 100% sulphuric acid

The plant has a capacity of 625t.d⁻¹ 100% sulphuric acid. The inlet SO₂ concentration bed 1 is 10.5%.





Best Available Techniques Booklets were first issued by Fertilizers Europe in 1995. Second revised edition 2000.

1. Production of Ammonia
2. Production of Nitric Acid
3. Production of Sulphuric Acid (in collaboration with ESA)
4. Production of Phosphoric Acid
5. Production of Urea and Urea-Ammonium Nitrate
6. Production of Ammonium Nitrate and Calcium Ammonium Nitrate
7. Production of NPK Compound Fertilizers by Nitrophosphate Route
8. Production of NPK Compound Fertilizers by Mixed Acid Route



Avenue E. van Nieuwenhuyse 4/6
B-1160, Brussels, Bélgica
Tel: +32 2 675 3550
Fax: +32 2 675 3961
main@fertilizerseurope.com

www.fertilizerseurope.com

twitter.com/FertilizersEuro



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Group Fertilizers Europe



Fertilizantes y fertilización

Arnold Finck

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Versión española por

D. Valentín Hernando Fernández

Profesor de Investigación de C.S.I.C.

Director del Curso Internacional de Fertilidad de suelos
y Nutrición vegetal

Dña. María Teresa Pardo Fernández

Colaborador Científico del C.S.I.C.

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debe realizarse de modo que las sustancias nutritivas alcancen la zona radicular y el producto consiga un efecto óptimo.

6.1.1 Transporte, almacenamiento y mezcla de los abonos sólidos

Durante la fabricación, los abonos son sometidos a un proceso de « *acondicionamiento*» que los convierte en productos de fácil y eficaz utilización; y no deben perder estas cualidades hasta el momento de su aplicación.

Para mantener sus propiedades se les da una forma granulada y se los espolvorea con determinados **aditivos**, sobre todo con sustancias no higroscópicas como la cal, tierra de diatomeas, etc. Estos productos pulverulentos impiden que las partículas de abono se adhieran unas a otras a causa de la humedad, que los gránulos se rompan bajo la presión y que el abono se deshaga en su totalidad.

The Basics of Zinc in Crop Production



International Fertilizer Development Center

The Basics of Zinc in Crop Production

R. G. Menon
**Research and
Development Division**

and

K. Z. Rahman
Outreach Division



International Fertilizer Development Center

Cover photo (zinc deficiency in corn plant) courtesy of Frit Industries/Pro•Sol.

The Basics of Zinc in Crop Production

Introduction

Zinc deficiency in soils and plants has become the most common of all the micronutrient deficiencies worldwide. Because zinc acts as a structural component of several enzymes in plants, an inadequate supply of zinc could result in serious physiological disturbances.

Functions of Zinc in Plants

Zinc is a bluish-white metallic element, which is recognized as one of the most required micronutrient fertilizers in the agricultural production system. Zinc has specific and essential physiological functions in plant metabolism. At least four enzymes contain zinc: carbon anhydrase (CA), alcohol dehydrogenase (ADH), copper-zinc-superoxide dismutase (Cu-Zn-SOD), and RNA polymerase. CA is localized in the chloroplasts and cytoplasm and is involved in photosynthetic CO₂ fixation. ADH plays an important role in anaerobic root respiration. Cu-Zn-SOD is involved in the detoxification of superoxide radicals (O₂⁻) and protection of membrane lipids and proteins against oxidation.

Various other enzymes involved in carbohydrate metabolism are Zn dependent. Zinc is important in protein synthesis and for the synthesis of tryptophan, a precursor for the synthesis of indole acetic acid.

Zinc Deficiency and Toxicity

Plants — Although used in small amounts by plants, Zn applications can produce spectacular results in Zn-deficient soils. Plants absorb Zn as a divalent cation (Zn²⁺). Zinc content of plants varies widely depending on the soil, climate, and plant genotype. The critical deficiency concentration (CDC) of Zn in leaves ranges from 15 to 30 mg/kg (Cakmak and Marschner, 1987), and the critical toxicity concentration (CTC) in leaves of crop plants ranges from 200 to 500 mg/kg.

In dicotyledons Zn deficiency results in short internodes (rosetting), formation of small leaves, stunted growth, and chlorosis of younger leaves. With increasing severity of the deficiency, leaves die

and fall off. In monocotyledons, interveinal chlorosis and violet-red spot-like discoloration of leaves are characteristics of Zn deficiency.

Plants particularly sensitive to Fe will become chlorotic if Zn is in excess. Crops that are sensitive to Zn deficiency include maize, rice, field beans, flax, apples, citrus, peaches, and pears. Crops that are moderately tolerant to Zn deficiency include wheat, barley, sorghum, soybeans, tomato, potato, sugar beet, cotton, and clover. Alfalfa, carrots, oats, peas, and rye are tolerant to Zn deficiency.

Zinc in Soils

Zinc occurs chiefly as the sulfide mineral sphalerite (ZnS). Zinc does not form independent silicates or generally occur to any great extent in quartz and feldspars (Lindsay, 1972). It also occurs as trace constituents of hydrous oxides of iron and manganese. Zinc forms silicates, oxides, carbonates, etc., but these are not stable.

Available Zinc

Most of the total Zn in soils exists in insoluble forms that contribute little to plant uptake. Soil Zn can be divided among generalized pools of plant availability. These are (Pickering, 1981):

Water-soluble pool: Zn present in soil solution.

Exchangeable and surface-adsorbed pool.

Organic pool: Zinc incorporated in organic matter in the soil.

Pool of metal oxides and carbonates.

Pool of primary and secondary minerals.

Water-soluble and exchangeable pools of Zn are considered readily available to plants. Organic Zn is also considered bioavailable. The carbonate pools are potentially available. Water-soluble and exchangeable pools are related to the intensity factor and form the basis of soil tests (Levesque and Mathur, 1988).

The amounts of bioavailable Zn are very small compared with the total Zn content of soils. In Indian soils, for example, bioavailable Zn forms no more than 1% of the total Zn (Katyal et al., 1982).

Geographic Distribution of Zn Deficiency

Zinc deficiencies are more common worldwide than those of any other micronutrients. The Zn status of the soils of some of the largest areas of the tropics, e.g., Congo Basin, Indochina Peninsula, Amazon Basin, and the Llanos has not been studied in detail. It is possible that soils may be deficient in zinc in these areas (Welch et al., 1991). However, zinc deficiency has been observed in the central plateau of Brazil, Colombia, and Peru (Jones, 1982). Zinc deficiency is found more frequently in the arid and semiarid regions of India and Thailand than in the humid and subhumid areas (Katyal and Vlek, 1985). Zinc deficiency has also been reported in the soils of the northern and central plains of West Java (Indonesia), the tropical soils of Taiwan, the poorly drained calcareous paddy soils of China, and in Sri Lanka (Matale). Sillenpää (1982) carried out a survey of the Zn status of soils globally and found that of all the countries surveyed, only Belgium and Malta did not report zinc deficiency (**Table 1**). Iraq, Turkey, Pakistan, and India had the lowest levels of zinc in soils. Brazil, Chad, Nigeria, and the Philippines have the most documented areas of zinc deficiencies (Sillenpää and Vlek, 1985).

In Africa, zinc deficiencies are widespread, in areas from Swaziland to Kenya and Uganda, including northern Zambia, Malawi, Tanzania, the west coast of Guinea, Cameroon, and Chad. Deficiencies have been reported in Côte d'Ivoire, Egypt, Ethiopia, Nigeria, Sierra Leone, Sudan, and Tanzania (**Figure 1**). Countries with zinc deficiencies in Asia include Bangladesh, Burma, India, Indonesia, Iraq, Japan, Korea, Lebanon, Nepal, Pakistan, Philippines, Syria, Thailand, Taiwan, Turkey, and extensive areas of China (**Figure 2**). Zinc deficiencies also have been reported in Finland, France, Hungary, Ireland, Italy, Switzerland, Sweden, and the United Kingdom (**Figure 3**) (Sillenpää, 1982). Zinc deficiencies are reported in Argentina, Brazil, Colombia, Ecuador, Mexico, and Peru in Latin America (**Figure 4**). Zinc deficiencies are also widespread in western Australia (Donald and Prescott, 1975), including Queensland, South Australia, Victoria, New South Wales, and parts of southern New Zealand (**Figure 2**). In the U.S.A., zinc deficiencies have been reported in the western, central, southern, and eastern regions of the United States although the deficiencies may be confined to small areas (**Figure 5**). The northeastern part of the United States has the lowest recorded incidence of zinc deficiency (Kubota and Allaway, 1972; Welch et al., 1991).

Factors Affecting Availability and Movement of Zinc

Plants absorb Zn mainly in the form of the ion Zn^{2+} . There is some evidence, however, that several Zn-organic complexes may also be absorbed by the roots (Kabata-Pendias and Pendias, 1984).

The plant availability of Zn is conditioned by a number of soil and environmental factors. These include:

Soil Parent Material — Parent materials have a great effect on the Zn content of soils. Basic rocks such as basalt and gabbro contain more Zn than acid-eruptive rocks, metamorphic rocks, or sedimentary rocks such as sandstones and limestones.

Soil pH — Availability of Zn decreases with increases in soil pH. Most pH-induced deficiencies occur within the range of pH 6.0 to 8.0. Alkaline soils are often Zn deficient even though total Zn content is relatively high.

Climate — Low temperatures and low light intensities reduce Zn uptake by plants. This may be due to restricted root development and decreased microbial decomposition of organic biomass at cool temperatures.

Interactions With Other Elements

Zinc interacts with various essential plant nutrients and other elements in soil and in plants.

Zinc Interaction With Other Nutrients

Zinc interacts with phosphorus, nitrogen, iron, calcium, copper, and manganese.

Zinc-Phosphorus — The antagonism between P and Zn has been researched extensively. The interaction is usually described as P-induced Zn deficiency. Beans, maize, potatoes, soybeans, sorghum, flax, citrus, rice, wheat, tomatoes, and hops have been reported to have experienced P-Zn interactions with a consequent detrimental effect on plant growth (Murphy et al., 1981). The most adverse effects occur when high levels of P are applied to Zn-deficient or higher pH soils.

Zinc-Iron — The metabolic function of Fe in plants is related to the supply of Zn. Increases of Zn in the soil depresses uptake of Fe by plants. Likewise, Zn deficiency increases Fe uptake by certain plants (Francois and Goodwin, 1972), sometimes to toxic levels (Adams and Pearson, 1967).

Zinc-Copper — High Zn availability in the soil can accentuate Cu deficiencies (Haldar and Mandal, 1981). Since Cu and Zn are presumably absorbed through the same mechanism, each competitively inhibits the uptake of the other (Bowen, 1979).

Zinc-Manganese — Zinc and Mn are antagonistic, and Mn uptake by plants is reduced with application of Zn fertilizers (Haldar and Mandal, 1981).

Zinc-Boron — Zinc fertilization may decrease B accumulation and reduce the risk of B toxicity in plants (Graham et al., 1987).

Zinc Interaction With Other Trace Elements

Zinc also interacts with other nutrients and heavy metals such as lead, chromium, selenium, and cadmium in soils. For example, application of Zn markedly reduced Cd concentration in wheat grown on soils of marginal Zn status (Tiller et al., 1993).

Zinc Fertilizers and Correction of Deficiencies

Evaluation of Zinc Availability to Plants

Zinc, like other nutrients, should be available in adequate amounts for the proper growth and development of plants. A soil test is a reasonably effective method for determining whether the soil has enough plant-available Zn to satisfy crop needs. The actual uptake of Zn can be more accurately assessed by plant tissue analysis.

Soil Test and Plant Analysis

The soil tests can often predict the possibility of zinc deficiency or toxicity occurring in the plants and provide information about the amount of Zn to be applied to correct deficiencies. Plant analysis provides information about the ability of the plants to absorb the nutrient from the soil and the concentration of the nutrient in plant tissues. Soil tests and plant analyses complement each other to help develop reliable fertilizer recommendations.

The plant analysis data will indicate the deficiency, sufficiency, or excess of Zn in the plants. For example:

Crop and Plant Part	Nutrient Status		
	Low	Sufficient	High
	(mg Zn/kg oven dry wt)		
Barley top	<15	15-70	>70
Maize top	<20	20-60	>60
Rice leaf	20-24	25-50	>50
Soybean leaf	10-20	21-50	51-75
Wheat (plant)	<15	15-70	>70
Tomato leaf	18-19	20-50	>50
Apple leaf	15-19	20-100	>100
Sorghum (aboveground)	<30	30-60	>60

Correction of Deficiencies

With intensification of crop production, removal of nutrients from the soil occurs at a rapid rate. When NPK fertilizers are used for some time, other deficiencies begin to develop and Zn is the one that often develops a deficiency after N, P, and K.

Many organic compounds, organic complexes such as ligninsulfonates, and synthetic chelates are used to correct Zn deficiency.

Zinc Fertilizers

Several fertilizers are available and inexpensive enough to use on crops in the market (**Table 2**). In addition to the manufactured compounds, animal manures and sewage sludge contain appreciable amounts of Zn and can also be used to correct Zn deficiencies. Sewage sludge, for example, may contain 150 to 12,000 mg Zn/kg. A typical sewage sludge may contain 5,000 mg Zn/kg dry weight (University of Illinois, 1975).

Zinc fertilizers can be grouped into four classes:

Inorganic fertilizers.

Synthetic chelates.

Natural organic complexes.

Slow-release fertilizers.

Inorganic Zn Sources — Inorganic sources of Zn include carbonates, chlorides, nitrates, oxides, and sulfates of Zn. Zinc sulfate is the most common source of Zn used in crop production. Historically, the basic raw material for the production of zinc sulfate has been slag and flue dust from zinc, copper, and lead smelter. These industrial wastes are treated with sulfuric acid to produce zinc sulfate. However, U.S. Federal and state environmental regulations have classified certain smelter slags and flue dusts as hazardous wastes, thus prohibiting their use in agriculture. Moreover, environmental regulations regarding sulfur dioxide and particulate emissions from smelters have resulted in the closure of many smelters. As a result, the availability of zinc-rich smelter slags and flue dust has decreased. Consequently, zinc sulfates are increasingly being prepared by reacting metallic zinc with sulfuric acid, which is a much more expensive method of producing Zn sulfate. Zinc sulfate is a white, finely divided crystal, sold in both crystalline and granular forms. Zinc sulfate monohydrate ($\text{ZnSO}_4 \cdot \text{H}_2\text{O}$) has 36% Zn, and heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) has 22% Zn. Both are soluble in water.

Zinc oxide (ZnO) is a white or yellowish amorphous powder. It is prepared by roasting naturally occurring mineral sphalerite (ZnS) or from zinc-rich smelter baghouse and flue dusts. ZnO contains 80.3% Zn. ZnO is not very water-soluble.

Zinc oxysulfate is a mixture of ZnO and ZnSO_4 . Zinc oxysulfate is made by partial acidulation of ZnO with sulfuric acid. The ratio of oxide to sulfate and the amount of water-soluble Zn in the product are directly related to the degree of acidulation. Depending on the source of Zn and the method of processing, total Zn content in Zn oxysulfate may vary from about 18% to 60% but averages 52%. About 35% to 50% of Zn in granular Zn oxysulfate should be in water-soluble form (ZnSO_4) to be effective for crops. However, there are no labeling requirements for water solubility of the micronutrient in the fertilizer. The U.S. uniform state government regulations require only that the total amount of the micronutrient be guaranteed and labeled on each bag/container. Zinc oxysulfate is usually sold as gray-brown granules.

Other zinc fertilizer products include metal ammonia complexes such as ammoniated ZnSO_4 solution, which contains 10% N, 10% Zn, and 5% S; Zn ammonium nitrate (15% Zn); and zinc nitrate, which are used in liquid form in advanced agricultural systems in the United States, Canada, and Western Europe.

Heavy Metal Contaminants — As previously indicated some industrial byproducts such as smelter slags and hazardous waste K061 flue dusts used in the preparation of ZnO and Zn oxysulfates may contain heavy metal contaminants such as cadmium (Cd), chromium (Cr), nickel (Ni), and lead (Pb). Concentrations of these heavy metals are highly variable. Some of these heavy metals, especially Cd and Pb, are highly toxic. Though there is no definite rule, industry usually controls Pb content at not more than 3% and Cd at not more than 0.03% by weight. However, there are no labeling requirements for heavy metals in micronutrient fertilizers. Heavy metals persist for decades and perhaps for centuries after they are added to the soil. Fortunately, they form insoluble compounds, which are not taken up by plants.

Cadmium is toxic to higher animals at high levels causing neuropathological symptoms and renal dysfunction. The balance of other minerals such as phosphorus and calcium in the body is also disturbed. Exposure to low doses of Cd is suspected to cause cancer, genetic ill effects, and hypertension. Tolerable daily Cd intake for humans is 1 g Cd per kilogram body weight.

However, because micronutrients are applied in very small quantities, inputs of contaminant heavy metals to the soil would be very low. For example, application of 5 kg/ha Zn as $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ containing 100 mg Cd/kg will result in the addition of only 1.38 g Cd/ha. Likewise, applying 10 kg ZnO containing 10 mg Cd/kg will add only 0.1 g Cd to the soil. Mortvedt (1985) has shown that concentrations of Cd in maize forage were not affected by Zn fertilizers containing 1 to 2,165 mg Cd/kg. However, Cd uptake by Swiss chard increased in an acid soil but not in an alkaline soil. These and similar studies suggest that plant uptake of heavy metals from industrial byproducts used as fertilizer is likely to be low if normal processing procedures and normal application rates are used. It is also important to remember that all safety precautions are to be taken while handling and applying fertilizers containing hazardous materials.

Synthetic Chelates — Synthetic chelates are produced by combining a chelating agent with a metal cation. The most common synthetic chelating agent used is ethylenediaminetetraacetic acid (EDTA). Zn EDTA is a finely divided or granular white material, which contains 9% to 14% Zn and is very stable.

Natural Organic Zn Complexes — Natural organic complexes are produced by reacting Zn with byproducts of the wood pulp industry, mainly lignosulfonates, phenols, and polyflavonoids. Zinc

lignosulfonates contain 5% to 12% Zn and Zn polyflavonoids, 7% to 10% Zn. These compounds are less stable than chelates and tend to form insoluble salts more quickly than chelates.

Slow-Release Zn Fertilizers — These included frits, coated fertilizers, Zn metal alloys, and Zn minerals. Zinc frits are prepared by mixing powdered silicates and micronutrients including Zn sulfate in proper proportion and melting the mixture in a furnace. Commercially available frits contain copper, boron, iron, manganese, and molybdenum in addition to Zn. Frits are usually sold as finely ground, brown, powdery materials. They are slowly soluble in water; the rate of dissolution is controlled by the particle size and composition of the matrix. Frits usually contain 7% to 9% Zn. Zn metal alloys are produced by smelting Zn with different metals. When they solidify they form mixed crystals, which are pulverized and used as fertilizer.

Other slow-release Zn fertilizers include Zn-ammonium phosphates (ZnNH_4PO_4), sulfur-coated ZnSO_4 , and mineral sphalerite (ZnS).

Farm Availability of Zinc Fertilizers — Zinc deficiencies in soils are becoming more common in many countries due to more intense agricultural cropping practices. No reliable data are available concerning global supply and demand of zinc fertilizer since its application rate is very small and the total consumption of zinc in a country profile is insignificant compared to the consumption of major fertilizers.

Several Asian, West European, and North American countries manufacture/process organic and inorganic zinc fertilizers of various grades in the form of fine powders, granules, and liquids and as components of multiple nutrient fertilizers. Most production is concentrated in the United States and Western Europe, and these fertilizers are available under different company trade names. Some of the companies and their products are listed in **Annex I**. Many industrial byproducts (industrial wastes) are being processed for manufacturing zinc fertilizer, and these products are available in many countries as cheaper sources of zinc. Because there are no labeling requirements to indicate the amount of water-soluble Zn or heavy metal contaminants, these products require analysis to ensure their suitability for farm use.

Application Methods and Rates

Recommended application rates for Zn are determined by the crop, Zn source, soil characteristics, method of application, and the severity of the Zn deficiency. Zn may be applied either to the soil as a basal dose or to the plant foliage as sprays. Foliar sprays are particularly useful for alkaline (high pH) soils.

Zinc in NPK Fertilizers — Zn, like other micronutrients, is applied in very small quantities, and therefore, uniform distribution in the field is difficult. Both granular and fluid NPK fertilizers are used as carriers for Zn. Zn may be combined with NPK fertilizers during the manufacture of NPK granular fertilizers or added during bulk blending. Zinc also may be coated on fertilizer granules or mixed with fluid fertilizers.

Comparison of Sources — The effectiveness of Zn fertilizers depends on several factors including water-soluble Zn content in the fertilizer, soil pH, method of application, and soil physical properties.

In general:

On acid soils, different Zn compounds including chelates are equally effective when applied as fine powder and incorporated into the soil.

ZnO is not very effective on soils with high pH.

Zn chelates are more available than inorganic compounds. Availability of Zn from lignosulfonate and polyflavonoids is between that of chelates and inorganic compounds.

Some studies suggest that 1 kg Zn applied as Zn EDTA is as effective as 10 kg Zn applied as ZnSO_4 . Others, however, show a ratio of 2 or 3:1 in favor of Zn EDTA.

Chelates are more effective when used on calcareous and alkaline soils.

On very acid soils, the efficiency of chelated Zn is the same as that of ZnSO_4 because the Zn may exchange with iron in the soil.

At high rates of application, Zn chelates and ZnSO_4 are equally effective. At lower rates, Zn chelate is more effective.

Agronomic effectiveness and cost per unit of Zn applied are primary factors to be considered when selecting the type of Zn compound to be used.

Soil Application

Zinc sulfate is the most common Zn source because of its wide availability, water solubility, and relatively low cost. Rate of application ranges from 4.5 to 34 kg Zn/ha. Zinc fertilizer is either broadcast, broadcast and incorporated into the soil, or banded. More Zn is needed to correct deficiencies on maize than on rice or sorghum. Zinc sulfate monohydrate is the most stable form in warm climates and is 100% water soluble.

Foliar Applications — Inorganic and organic sources of Zn may be used as foliar spray to correct Zn deficiencies. Foliar application is primarily used for tree crops.

Other Applications — Other application methods include seed coatings, root dips, and tree injections.

Residual Effects

Most of the zinc applied to soils reverts into plant-unavailable forms slowly when relatively large amounts of Zn are broadcast to correct deficiencies. The residual effect of applied Zn lasts for several years.

Toxic Effects — Since only small amounts of Zn are leached, reversion to unavailable forms is slow, and crop removal is small. Continued high application of Zn to the soil could raise Zn concentration to toxic levels; this is highly unlikely at normal rates. The U.S. Environmental Protection Agency (1983) has recommended that the total cumulative limits for Zn application to croplands are 280, 560, and 1,120 kg Zn/ha for soils with CEC levels <5, 5 to 15, and >15 cmol_c/kg, respectively, when sewage sludge is incorporated into the soil to correct Zn deficiencies.

Crop Response to Zinc Application

Spectacular increases in crop yields have been reported from the application of Zn to Zn-deficient soils. Hergert et al. (1984) have shown that application of as little as 0.11 kg/ha Zn band applied with a starter fertilizer on a Zn-deficient soil increased maize yield from 3,900 to 8,300 kg/ha.

Rice response to Zn, though not as dramatic as for maize, is significant in Zn-deficient soils. In Arkansas, application of 0.84 kg Zn/ha as Zn-EDTA increased rice yields from 3,584 kg/ha to 5,633 kg/ha. Application of 1.68 kg Zn/ha produced an additional yield of 3,091 kg/ha over yield with no Zn applied (Wells et al., 1973).

Significant increases in yield of grain sorghum have been reported from the application of Zn to nutrient-deficient soils. When 0.6 kg/ha Zn was broadcast and incorporated before planting, the yield of grain sorghum increased from 4,077 to 4,767 kg/ha. Increasing the rate to 2.2 kg Zn/ha increased the yield to 5,268 kg/ha (Follet et al., 1981).

Similar yield increases have been reported for soybean from Zn application to deficient soils in Kansas. Without Zn, the yield of soybeans was 2,016 kg/ha. Application of 2.2 kg Zn/ha increased yield by 1,075 kg/ha, and application of 4.5 kg Zn/ha increased yield by 1,344 kg/ha. Above 4.5 kg Zn/ha, there was a decrease in yield.

Significant increases in yield have been reported for other crops. Application of NPK fertilizers containing Zn to provide 3 kg Zn/ha increased the yield of dry beans from 12,300 to 16,700 kg/ha (Ellis et al., 1965).

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Table 1. DTPA Extractable Zn in Soils From Selected Countries

Country	No. of Samples Analyzed	Zn in Soils		
		Maximum	Minimum	Mean
		(mg/L)		
Argentina	119	12.00	0.41	2.03
Belgium	21	10.53	2.79	5.17
Brazil	71	123.90	0.20	3.81
Ecuador	16	2.90	0.24	1.41
Egypt	100	7.50	0.46	1.31
Ethiopia	54	9.90	0.49	2.07
Finland	94	13.13	0.34	2.17
Hungary	144	8.75	0.34	1.18
India	188	38.80	0.10	1.16
Iraq	119	3.50	0.07	0.28
Italy	118	47.50	0.17	2.31
Malta	25	39.40	2.02	10.29
Mexico	100	14.80	0.22	0.98
Nepal	50	6.70	0.11	0.75
New Zealand	14	5.10	0.28	1.45
Nigeria	42	3.10	0.28	0.78
Pakistan	156	12.10	0.10	0.82
Peru	13	30.20	0.42	3.66
Syria	20	7.40	0.10	1.21
Tanzania	5	0.10	0.06	0.09
Turkey	249	3.60	0.12	0.39

Source: M. Sillenpää, 1982.

Table 2. Some Sources of Fertilizer Zn

Sources	Formula	Percent Zn
Inorganic		
Zn sulfate monohydrate	$\text{ZnSO}_4 \cdot \text{H}_2\text{O}$	36
Zn sulfate heptahydrate	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	22
Basic Zn sulfate	$\text{ZnSO}_4 \cdot 4\text{Zn}(\text{OH})_2$	55
Zn chloride	ZnCl_2	47
Zn carbonate	ZnCO_3	52
Zn oxide	ZnO	60-78
Zn oxysulfate	$\text{ZnSO}_4 \cdot \text{ZnO}$	25-60
Synthetic Chelates		
Zn chelates	$\text{Na}_2 \text{ Zn EDTA}$	14
	Na Zn NTA	13
	Na Zn HEDTA	9
Organic Complexes		
Zn polyflavonoid		10
Zn ligninsulfonate		5

Table 3. Countries With Reported Zinc Deficiencies

Africa	Asia & Oceania	Europe	Latin America
Chad Côte d'Ivoire Egypt Ethiopia Guinea Nigeria Sierra Leone Sudan Tanzania Zimbabwe	Australia Bangladesh Burma China India Indonesia Iraq Japan Korea Nepal New Zealand Pakistan Philippines Syria Thailand Turkey	Finland France Hungary Ireland Italy Sweden Switzerland United Kingdom	Argentina Brazil Colombia Ecuador Mexico Peru

Figure 1

AFRICA

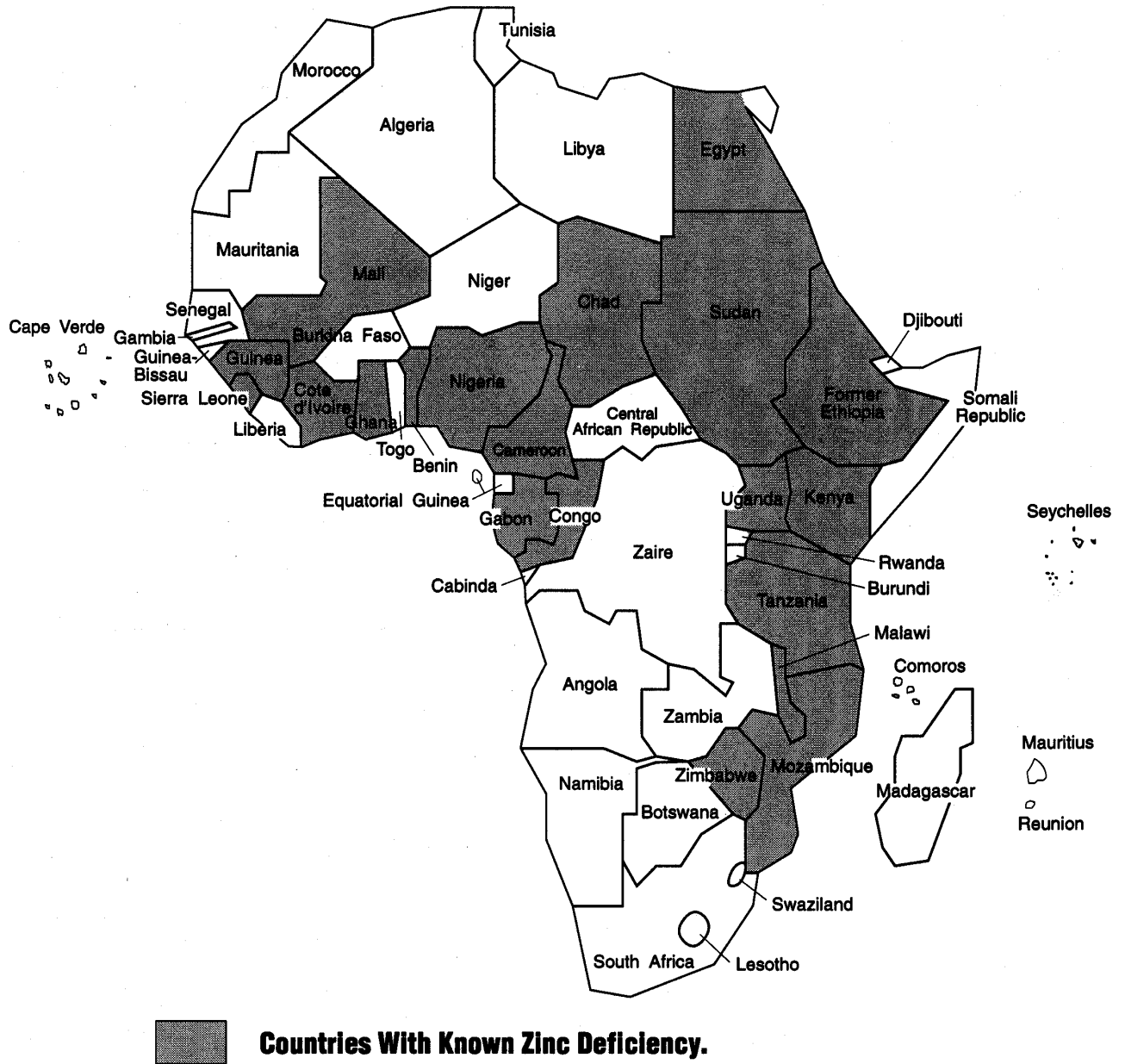


Figure 2

ASIA

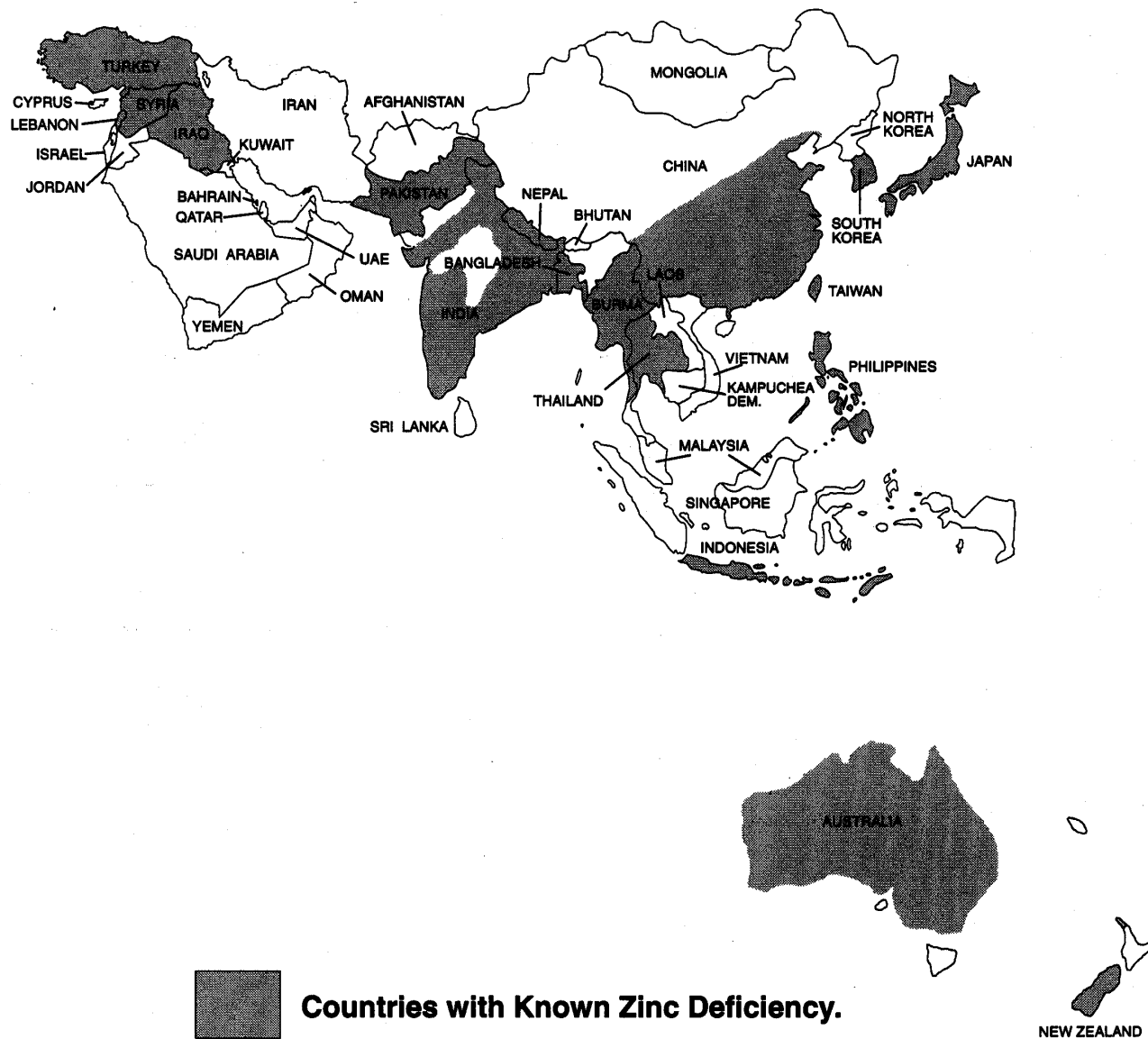


Figure 3

EUROPE

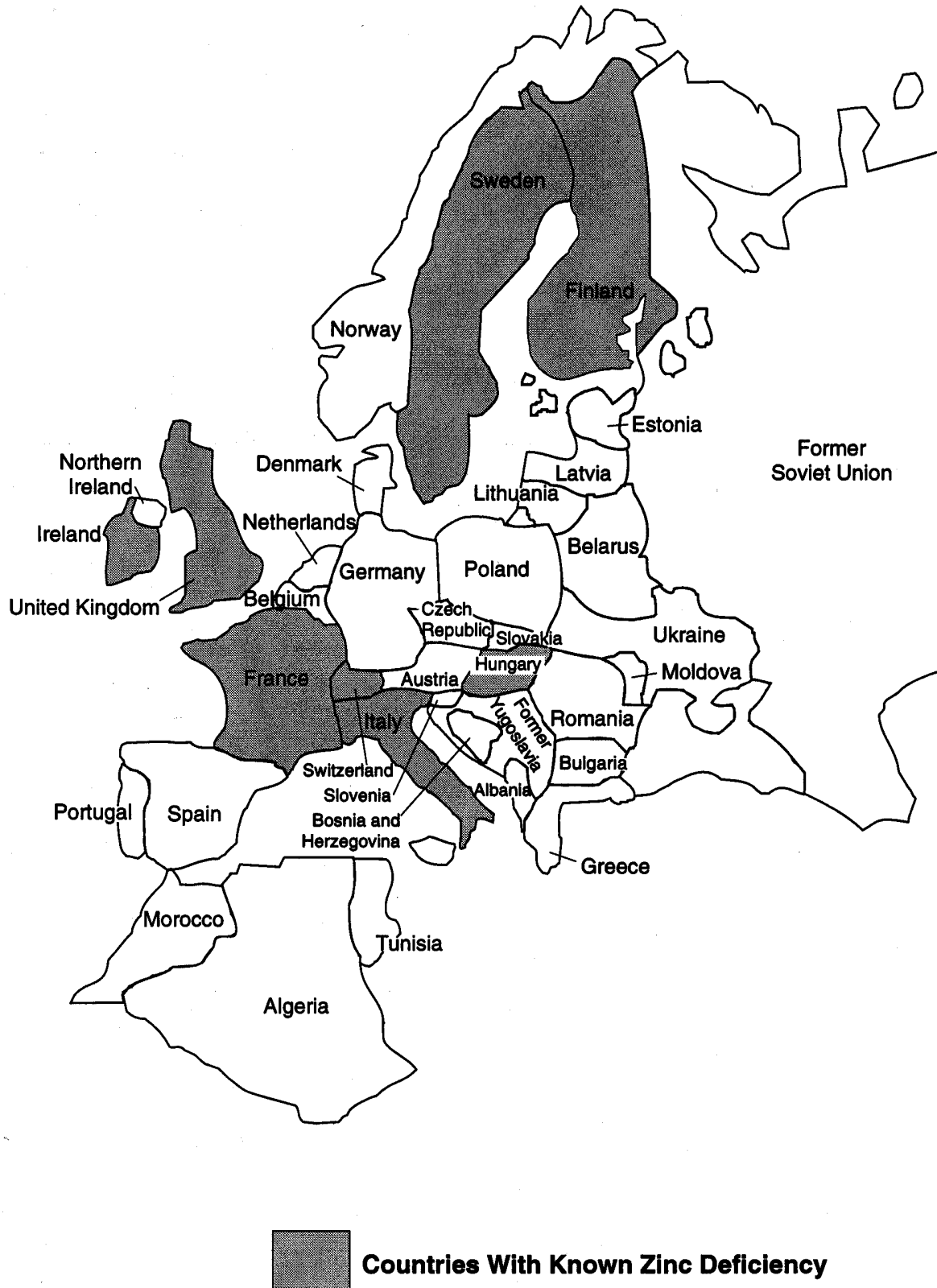


Figure 4

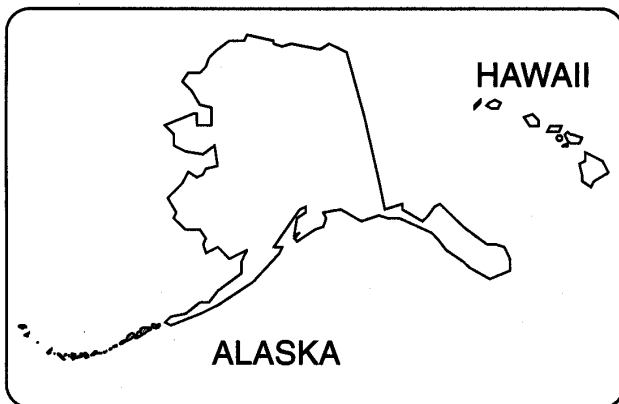
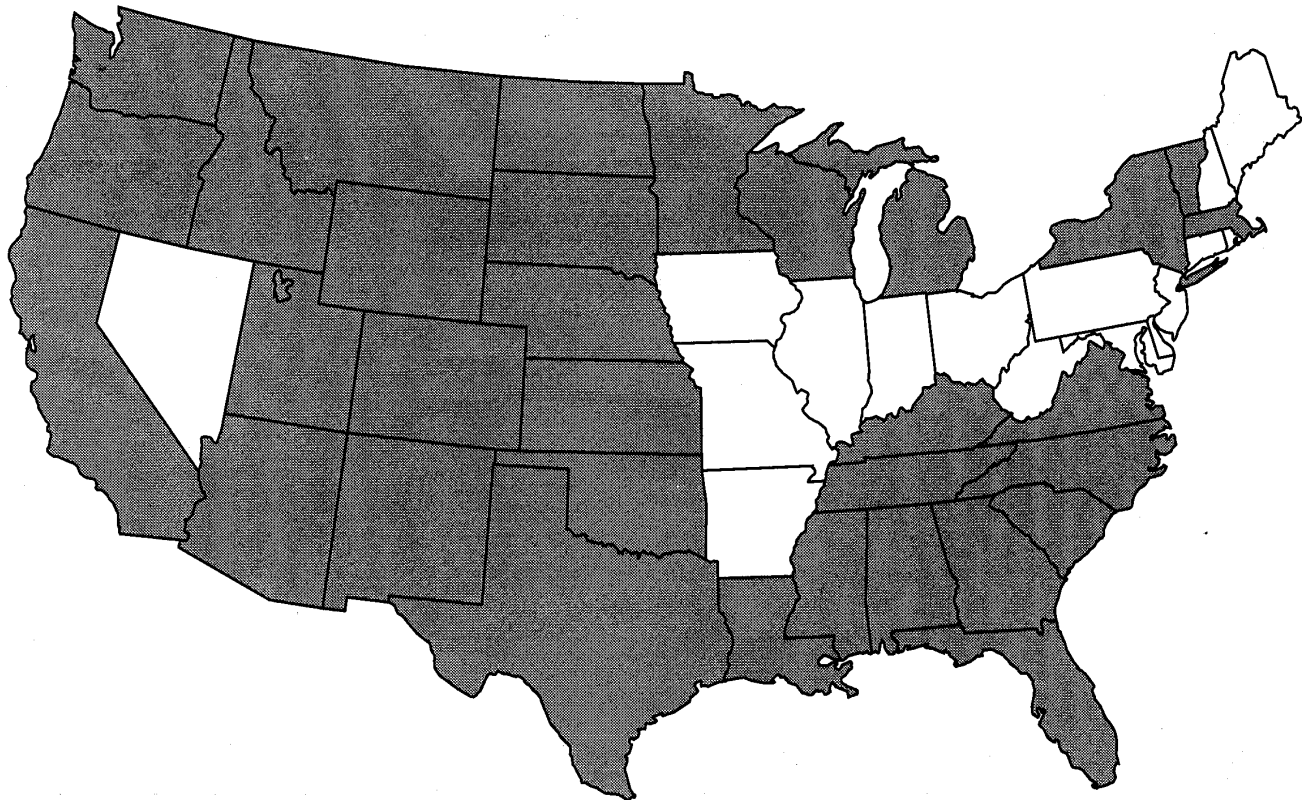
LATIN AMERICA



Countries With Known Zinc Deficiency

Figure 5

UNITED STATES OF AMERICA



States With Known Zinc Deficiency

Source: American Zinc Institute Inc., New York, N.Y...

Annex I

Commercial Zinc Products, Manufacturers, and Suppliers

Producer/Supplier	Product Trade Name		Description	Type
Australia				
Pasminco Metal-Ez Fertilizer Resdon Road Tasmania Telephone: (61-02) 784-921 Fax: (61-02) 784-930	Product trade name and description not available			
Tasbond LRL Ltd. 1027 Mountain Highway Bayswater, Victoria 3153 Telephone: (61-3) 685-6000 (61-3) 614-3569	Product trade name and description not available			
Austria				
AgroLinz P.O. Box 21 St. Peter Street 25 A4021 Linz Telephone: 43-732-5914 Fax: 43-732-3691	Folifert Super Volkorn	20-6-6+10% Mg, 1% Zn 15-5-18+2.5% MgO;Zn	Fine granular	
Belgium				
Ameco Belgium N.V. Louizastraat 39 2000 Antwerp Telephone: (32-3) 255-2556 Fax: (32-3) 232-3832	Product trade name and description not available			
MicroNutrient N.V. Frankrijklei 65 Bus 3 B2000 Antwerp Telephone: (32-3) 225-1400 Fax: (32-3) 234-1967	Product trade name and description not available			
Colombia				
Abonos Colombianos S.A. Carrera 9a. No. 74-08, Ofc 1003 Santa Fe de Bogota, D.C. Telephone: (57-1) 288-6100 Fax: (57-1) 285-7203 Telex: 044781	Not available	17-6-18+0.2% Mg, 0.2% B, 0.1% Zn	Granular	

Producer/Supplier	Product Trade Name	Description	Type
Monomeros Colombo Venezolanos S.A. (EMA) Planta via 40 Las Flores Apartado Aereo 3205 Barranquilla Telephone: (57-58) 565621 Fax: (57-58) 2811885;3420063 Telex: 31138 MCV Co	Not available	17-16-18+2% MgO, 1.5% S, 0.1% Zn, 0.2% B	Granular
		14-14-14+2% MgO, 0.1% Zn, 0.2% B, S	Granular
Czech Republic			
Synthesia AS, Zavod 01-Anorganika Zavod 01-Anorganika 53217 Pardubice-Semtin Telephone: (42-40) 493 Fax: (42-40) 46465 Telex: 196222	Not available	11-9-14+1.5% MgO, Zn, B, Cu, Mo	Granular
	Not available	15.50-7.50-10.0+3% MgO, Mo, B, Zn, Cu	Granular
Germany			
Aglukon Spezialdunger GmbH P.O. Box 190343 D-40522 Dusseldorf Telephone: 49-211-506 4221 Fax: 49-211-506 4249	Hortazon Micro	Multiple nutrient fertilizer with 0.5% Zn	Slow release
	Wuxal Micro	10-0-0+2% Fe, 2% Mn, 2% Zn EDTA chelated	Suspension
	Wuxal Micro Zn	10-0-0+1% Fe, 2% Mn, 3% Zn EDTA chelated	Suspension
Metalldunger Jost GmbH Box 2052 58590 Iserlohn Telephone: (49-2371) 948523 Fax: (49-2371) 948535	Excello-Bor	3% Zn	Granules
	Excello-granuliert	3% Zn	Granules
	Excello-5% Cu	3% Zn	Granules
	Excello-Manesium	1% Zn	Granules
	Excello-Mangan	0.5% Zn	Granules
	Excello-Zink	8% Zn	Granules
	Excello-Weide	3% Zn	Granules
	Radigen	0.5% Zn	Granules
	(All these products are Zn-metal alloys containing different micronutrients)		
	Folicin	Zn-EDTA chelate	Powder or liquid
Stahler Agrochemei GmbH & Co. KG Stader Elbstrasse 21683 Stade Telephone: (49-4141) 2016 Fax: (49-4141) 45540	Not available	14% Zn	Granular
	Not available	Compound micronutrient fertilizer with Zn	Granular
Greece			
Chemical Industries of Northern Greece SA P.O. Box 10183 54110 Thessaloniki Telephone: (30-31) 760403 Fax: (30-31) 760422	Not available	8-12-12+0.5% B, 0.2% Zn	Granular
	Not available	20-10-10+2% Zn SOP	Granular
	Not available	14-5-14+2% Zn	Granular
	Not available	24-0-0+1.5% Zn	Granular
	Not available	13.5-0-0+10 Zn	Powder
India			

Producer/Supplier	Product Trade Name	Description	Type
Aries Agro-vet Industries Pvt. Ltd. Aries House 24, Deonor Govandi East Bombay 400043 Telephone: (91-22) 556-4052 Fax: (91-22) 515-3038	Agromin Chelamin	Mixture of chelates containing Zn, Cu, Mn, and Fe 12% Zn EDTA	Powder Powder
Khatau Junker Ltd. Khatau House Mogul Lane, Mahim Bombay 400016 Telephone: (91-22) 444-9766 Fax: (91-22) 444-0826	Product trade name and description not available		
Nagarjuna Fertilizers and Chemicals Ltd. Nagarjuna Hills Panjaghutt Kakinada 533 003 Andhra Pradesh Telephone: (91-40) 227 589 Fax: (91-40) 226 788	Product trade name and description not available		
Italy			
Chemia S.P.A. Via Statale 327 44040 Dosso (Ferrara) Telephone: (39-532) 848477 Fax: (39-532) 848383	Nutrifix	13-5-38+B,Fe,Mg,Mn,Zn,Cu	Liquid
Mexico			
Grupo Bioquimicol Mexicano, S.A. de C.V. P.O. Box 238 Blvd. Jesus Valdez Sanchez 2369 Saltillo Coahuila 25290 Telephone: (52-84) 16-17-77 Fax: (52-84) 15-27-96	Poliquel Multi	4% Zn with other micronutrients	Liquid
	Poliquel Zn	8% Zn multichelated	Liquid
Netherlands			
B.V. Industrie-2 Handelonderneming Simonis P.O. Box 620 7000 AP Doetinchem Telephone: 31-83-40-33700 Fax: 31-83-40-44167	Product trade name and description not available		
Melchemie Holland B.V. P.O. Box 143 6800 AC Arnhem Holland Telephone: 31-85-45-1251 Fax: 31-85-42-5093	Product trade name and description not available		
New Zealand			

Producer/Supplier	Product Trade Name	Description	Type
Fernz Corporation Ltd. P.O. Box 759 Auckland Telephone: (64-9) 379-3001 Fax: (64-9) 366-1394	Not available	CoSO ₄ , ZnSO ₄	Granular
Pakistan			
Lyallpur Chemicals & Fertilizers Ltd. Lahore Road, Jaranwala District Faisalabad Telephone: (92-468) 310200 Fax: (92-468) 312628 Telex: 43373 LCF PK	Not available	Zinc sulfate	Powder
National Fertilizer Corporation of Pakistan 1st Floor Alfalalah Building (Tail Wing) Shahrah-e-Quaid-e-Azam Lahore Telephone: (92-42) 630-2904 Fax: (92-42) 630-2918 Telex: 44726 NFC PK	Not available	Zinc sulfate 21% Zn	Powder
South Africa			
Kynoch Fertilizer Ltd. P.O. Box 3836 Randburg 2125 Telephone: (27-11) 787-0419 Fax: (27-11) 789-5354	Not available Not available Not available Not available	6.3-21.5-7.6+0.5% Zn 8.6-29.3-10.4+0.5% Zn 6.7-22.9-16+1% Zn 3.8-28.0-0+0.5% Zn	Granular Granular Granular Granular
Sasol Fertilizers P.O. Box 1723 Randburg 2123 Telephone: (27-11) 886-3044 Fax: (27-11) 886-8643	Not available Not available Not available	6.3-21.5-7.6+0.5% Zn 21-16-0+0.5% Zn 21.5-19-5+0.5% Zn	Granular Granular Granular
United Kingdom			
C.M.I. Ltd. United House, 113 High Street Collingham, Newark Notts NG23 7NG Telephone: (10636) 89-2078 Fax: (10636) 89-3037	CM Zinc Superflor Mn	7% Zn 14% Zn EDTA	Liquid Powder
United States			
Agribusiness Supply Albany, GA	Agrinutrient Agristarter	36% Zn, Zn oxysulfate 10% Zn	Granular Liquid

Producer/Supplier	Product Trade Name	Description	Type
Albion Laboratories Inc. P.O. Box 750 101 N. Main Street Clearfield, UT 84015 Telephone: (801) 773-4631 Fax: (801) 773-4633	Albion Metalosates	6.8% Zn chelate	Liquid
Allied Colloids Inc. P.O. Box 820 2301 Wilroy Road Suffolk, VA 23439-0820 Telephone: (804) 538-3700 Fax: (804) 538-0204	Librel Zn Librel RMX8	14% Zn EDTA Multiple nutrient fertilizer with 2.6% Zn EDTA	Granule/powder Powder
Alpine Plant Foods Inc. 3185 Cline Road Corydon, IN 47112 Telephone: (812) 738-1333 Fax: (812) 738-1199	Liqui Cal	9% Zn chelate	Liquid
American Micro Trace Corporation 569 Central Drive, Suite 201 Virginia Beach, VA 23454 Telephone: (804) 463-5013 Fax: (804) 463-8156	Coarse Zink Super Fine Zink Super TEL Zn Zink-33 Zink-Gro Zink-Gro AS	35.5% Zn sulfate monohydrate 35.5% Zn sulfate monohydrate 33.5% Zn sulfate monohydrate 33.5% Zn sulfate monohydrate 35.5% Zn sulfate monohydrate 35.5% Zn sulfate monohydrate	Fine granular Powder Powder Granular Granular Fine granular
American Minerals Inc. P.O. Box 2005 Dunedin, FL 34697-2005 Telephone: (813) 734-3284 Fax: (813) 733-0503	Granusol	36% Zn.Zinc sucate	Granule
Arcadian Corp. 6750 Poplar Avenue, Suite 600 Memphis, TN 38138 Telephone: (901) 758-5200 Fax: (901) 758-5204	Liqui-zinc NZN	10%-12% Zn.Zn amine complex N + 5% Zn	Liquid
Bay Zinc Co., Inc. P.O. Box 167 301 W. Charron Rd. Moxee, WA 98936 Telephone: (509) 248-4911 Fax: (509) 248-4916	Blu-Min Blu-Min Blu-Min LHM	18% Zn.Zinc oxysulfate 10.5% Zn.Zinc sulfate 18% Zn.Zinc sulfate	Granular Liquid Granular
Chem One Corp. 15150 Sommermeyer Houston, TX 77041-5308 Telephone: (713) 896-9966 Fax: (713) 896-7540	Zinc	35.5% Zn.Zinc sulfate monohydrate	Powder/granular

Producer/Supplier	Product Trade Name	Description	Type
Chemical & Pigment Co. 600 Nichols Road Pittsburg, CA 94565 Telephone: (510) 689-2030 Fax: (510) 458-2410	Meteor	52% Zn.Zinc sulfate basic	Powder
	Meteor	36% Zn.Zinc sulfate monohydrate	Granular
	Meteor	62% Zn.Zinc chloride	Solution
Chemical Dynamics Inc. P.O. Box 486 Plant City, FL 33564-0486 Telephone: (813) 752-4950 Fax: 9813) 752-8639	Dyna Gold	3.6% Zn, 2.9% Mn, 3.5% S	Liquid
	MZ Mix		
	Dyna Gold	1.6% Fe, 2% Mn, 2.4% Zn, 3.5% S	Liquid
Conklin Co., Inc. P.O. Box 155 551 Valley Park Dr. Shakopee, MN 55379 Telephone: (612) 445-6010 Fax: (612) 496-4285	Dyna Gold	7% Zn	Liquid
	Zinc		
	Feast	9% Zn EDTA fully chelated	Liquid
Cornbelt Chemical Company P.O. Box 410 North Highway 83 McCook, NE 69001 Telephone: (308) 345-5057 Fax: (308) 345-3401	Feast CropMix	4% Zn, 1% Fe, 1% Mn EDTA, HEDTA fully chelated	Liquid
	CornGro	3.5% Zn, 0.6% Mn, 0.4% Cu EDTA fully chelated	Liquid/powder
	Super Blend Plus	3% Zn, 1% Fe, 1% Mn, 0.5% Cu EDTA fully chelated	Liquid/powder
CoZinco, Inc. 7400 Jefferson Avenue Denver, CO 80235 Telephone: (303) 969-9414 Fax: (303) 989-0322	CoZinCo	35.5% Zn.Zinc sulfate	Granular
	CoZinCo	12% Zn	Liquid
	CoZinCo SD36	35.5% Zn.Zinc sulfate	Powder
	CoZinCo	31% Zn.Zinc sulfate	Granular
Crystal Chemical Inter-America 10303 NW Freeway Suite 512 Houston, TX 77083 Telephone: (713) 956-6196 Fax: (713) 956-6835	Kelaplex Zinc	14% Zn fully chelated	Soluble powder
	Kelaplex Zinc	79% Zn.Zinc oxide	Liquid
	Kelaplex Zinc	36%, 20% Zn.Zinc sulfate	Soluble powder
	Kelaplex Zinc	10%, 12% Zn.Zinc sulfate	Solution
	Zinquel	6.5% Zn, 4% S fully chelated	Liquid
	Zinc	75% Zn.Zinc oxide	Spray grade
Farmland Industries, Inc. P.O. Box 7305 Kansas City, MO 64116 Telephone: (816) 459-6000 Fax: (816) 459-5913	Farmland	Ammoniated Zn chloride, ammoniated Zn sulfate	Liquid
	Farmland	10%-20% Zn	Liquid
	Farmland	9% Zn chelate	
	Farmland	20%-35.5% Zn.Zinc sulfate	Granular
Fertilizer Corporation of America 9370 Sunset Drive #A-240 Miami, FL 33173 Telephone: (305) 595-6738 Fax: (305) 595-9367	Balance 18ZN	18% Zn, 12% Fe, 1% Mn, 7% S	Granular blend
	Balance 36ZN	36% Zn, 6% S	Granular
	Balance	36% Zn, 17% S	Prills
	36ZnSO ₄		
	Microfol Zinc	7% Zn, 4% S chelated	Liquid
	Microfol Zinc	10% Zn, 5% S chelated	Liquid

Producer/Supplier	Product Trade Name	Description	Type
Frit Industries P.O. Box 1589 Ozark, AL 36361-1589 Telephone: (334) 774-2515 Fax: (334) 774-9306	F420G	20% Zn	Granular
	F317G	36% Zn	Granular
	F305G	20% Zn micronutrient mixture	Granular
	F307G	20% Zn micronutrient mixture	Granular
	CZN	10% Zn chelate	Granular
	Zn chelate	7% Zn	Liquid
	Zn chelate	10% Zn	Liquid
	Pro. sol.	25% Zn Zn citric acid chelate	Powder
Georgia Pacific Corp. P.O. Box 1236 300 W. Laurel St. (98225) Bellingham, WA 98227 Telephone: (800) 385-4348 Fax: (206) 676-7217	Zinc KE-MIN	14% Zn	Powder
	Zinc KE-MIN	5.6% Zn	Liquid
	Z-M-KE-MIN	3.2% Zn, 1.6% Mn	Liquid
J. M. Huber Corp. P.O. Box 4005 3150 Gardner Expwy. Quincy, IL 62305 Telephone: (217) 224-1100 Fax: (217) 224-7957	Zinc	36% Zn.Zinc sulfate	
	Zinc	72% Zn.Zinc oxide	
Hydro Agri North America Inc. 100 N. Tampa St., Suite 3200 Tampa, FL 33602 Telephone: (813) 222-5700 Fax: (813) 875-5735	Not available	52% Zn.Zinc sulfate, basic	Powder
	Not available	36% Zn.Zinc sulfate	Spray dried
	Not available	26% Zn.Zinc sulfate-iron sulfate	Granular/powder
	Not available	12% Zn.Zinc sulfate	Solution
	Meteor	Zinc sulfate	
Imperial Products, Inc. 1071 W. Morse Blvd. Winter Park, FL 32789-3747 Telephone: (407) 628-1494 Fax: (407) 628-3676	IPI Zinc	15% Zn EDTA	Powder
	IPI Zinc	36% Zn, 18% S.Zinc sulfate monohydrate	Powder, granular
	Not available	80% Zn.Zinc oxide	Wettable powder
	Not available	36% Zn.Zinc sulfate monohydrate	Granular
Lidochem Inc. Village Park Office Complex 20 Village Court Hazlet, NJ 07730 Telephone: (908) 888-8000 Fax: (908) 264-2751	Lidoquest	Zinc ethylenediaminetetraacetic acid 14% Zn	Powder
	Zinc 14P		
	Zinc sulfate	35% zinc	Fully soluble
Mineral Research & Development Division of Chemical Specialist Inc. One Woodlawn Green Suite 250 Charlotte, NC 28217 Telephone: (704) 525-2771 Fax: (704) 527-8232	Mineral Research	17% Zn.Zinc nitrate	Liquid
	Mineral Research	23% Zn.Zinc nitrate	Flakes
	Mineral Research	24%, 28%, & 31% Zn.Zinc chloride	Liquid
		46.6% Zn, 80% solids zinc carbonate	
	Mineral Research	47%, 49% Zn.Zinc chloride anhydrous	Dustless
	Mineral Research	58% Zn.Zinc carbonate	
	Mineral Research		Dry

Producer/Supplier	Product Trade Name	Description	Type
Monterey Chemical Co. (Trader) P.O. Box 5317 Fresno, CA 93755 Telephone: (209) 225-4770 Fax: (209) 225-1319	Hamp-Ene Zinc	6% Zn EDTA chelate	Liquid
	Hamp-Ene Zinc	14% Zn EDTA chelate	Powder
	Monterey Mix	3% S, 18.5% Zn, 7% Mn	
	Monterey Mix	22% Zn, 10% Fe	
	Monterey Mix	52% Zn.Zinc oxysulfate	Powder
	Monterey Zinc	72%, 75% Zn.Zinc oxide	Suspendable powder
	Monterey Zinc	31% Zn.Zinc sulfate	Granular
	Monterey Zinc	36% Zn.Zinc sulfate	Powder/granular
	ULB Urea	20% Zn + ultra-low biuret urea	
Old Bridge Chemical Inc. P.O. Box 194 Old Bridge, NJ 08857 Telephone: (908) 727-2225 Fax: (908) 727-2653	Zinc	30% Zn.Zinc chloride	Solution
	Zinc	13% Zn.Zinc sulfate	Solution
	Zinc Sulfate	35.5% Zn	Powder
Plant Health Technologies Crop Protection Products P.O. Box 15057 Boise, ID 83715 Telephone: (208) 345-1021 Fax: (208) 345-1032	Folo Spray Neutral	52% Zn	Slowly soluble
	Zinc		
	Folo Spray Nutra Wet	NPK + 20% Zn	-
	Folo ZnK		
Prince Agri Products P.O. Box 1099 Quincy, IL 62306 Telephone: (217) 222-8854 Fax: (217) 222-5098	N-Zn-B	14-0-22 + 15% Zn, 2% Mn	-
		24-2-6, 5% S, 10% Zn	-
	Not available	36% Zn.Zinc sulfate 72% Zn.Zinc oxide	Granular/powder -
PureGrow Co. 1276 Halyard Drive West Sacramento, CA 95691 Telephone: (916) 372-7184 Fax: (916) 372-7205	LeafLife Heads-up	5% N, 5% Ca, 2.5% Zn	
	LeafLife Super	10% N, 10% Zn	Liquid
	Zinc 10		
	Super Sol-U K	12-8-30 + 4% Zn	Solution
	Super Sol-U Phos	12-46-4 + 2.75% S, 3% Zn	Solution
Ruffin Micronutrients P.O. Box 940 Dodge City, KS 67801 Telephone: (800) 535-7479 Fax: (316) 225-7035	Ruffin Tuff 5-22-0	1.0% Zn	Liquid
	Ruffin Tuff 10-0-0	10% Zn	Granular/liquid
	Ruffin-Ready-Zn	10% Zn	Liquid
	Special crop mix 1	5% Zn	Liquid
Shield-Brite Division of Pace International LP P.O. Box 519 500 7th Ave S. Kirkland, WA 98083 Telephone: (206) 827-8711 Fax: (206) 822-8261	NutraSpray Zinc 50	Not available	Wettable powder
	NutraSpray	17.5% Zn, Mn 4%, Cu 4%	Wettable powder
	NutraSpray	18.5% Zn, Mn 7%	Wettable powder
	NutraSpray	25% Zn, Mn 25%	Wettable powder
	Zintrac 8	40% Zn	Suspension
	Zinphos 7	28% phosphoric acid, 9.4% Zn	Liquid concentrate

Producer/Supplier	Product Trade Name	Description	Type
Sims AG Products, Inc. 3795 County Road 29 Mt. Gilead, OH 43338 Telephone: (419) 946-2015 Fax: (419) 946-6571	BinBuster Zinc 20%	20% Zinc oxysulfate	Granular
	BinBuster Zinc 31%	31% Zinc oxysulfate	Granular
	BinBuster Zinc 36%	36% Zinc oxysulfate	Granular
Traylor Chemical & Supply Co., Inc. P.O. Box 547937 Orlando, FL 32854-7937 Telephone: (407) 422-6151 Fax: (407) 423-5316	Hapta-Gro Liquid	9% Zn, 4% S	Liquid
	Metagro Corn Mix	5% Zn, 1% Mn, 1% Cu, 4% S	Liquid
	Metagro	10% Zn complex	Granular
	Traylor Zinc	50%-65% Zn.Zinc oxide	
	Traylor Zinc	52%, 78%, 80% Zn.Zinc oxide	
	Traylor Zinc	20%, 36% Zn.Zinc oxide	Granular/powder
	Traylor Zinc	35.5% Zn.Zinc sulfate	Wettable powder
	Traylor Zinc	10% Zn.Zinc ammonium sulfate	Granules
	Traylor Zinc	14% Zn chelate	Granular/powder
	Traylor Zinc	17% Zn, 7% N.Zinc nitrate	Liquid
	Zinc Ammonium Chloride Sulfate	13% N, 4.5% S, 15% Zn	Powder
Zinc Corporation of America 300 Frankfort Road Monaca, PA 15061 Telephone: (412) 774-1020 Fax: (412) 773-2269	Kadox 911; 920; 930	80% Zn	Powder/granular
	Zinc Sulfate	11% Zn.Zinc sulfate	Liquid
	Zinc Oxide	79.5% Zn	Powder/granular
	Equidae Zinc Oxide	70% Zn	Powder

Source: *Farm Chemicals Handbook*, 1995.

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International Fertilizer Development Center
P.O. Box 2040
Muscle Shoals, Alabama 35662, U.S.A.

Steam Turbine Cogeneration

Keith Quach
 PERRL Manager
 Environment Canada
 Ottawa, Ontario

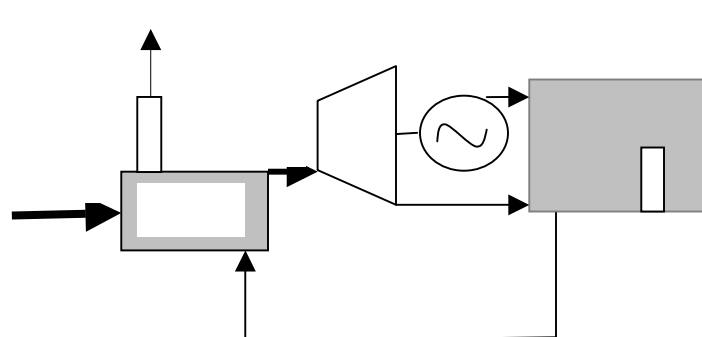
Gordon Robb
 President
 COGEN CHP Canada Association
 Ottawa, Ontario

ABSTRACT:

Steam turbines are widely used in most industrial facilities because steam is readily available and steam turbine is easy to operate and maintain. If designed properly, a steam turbine co-generation (producing heat and power simultaneously) system can increase energy efficiency, reduce air emissions and qualify the equipment for a Capital Cost tax Allowance. As a result, such a system benefits the stakeholders, the society and the environment. This paper describes briefly the types of steam turbine classified by their conditions of exhaust and review quickly the fundamentals related to steam and steam turbine. Then the authors will analyze a typical steam turbine co-generation system and give examples to illustrate the benefits of the System.

INTRODUCTION

Combined Heat and Power (CHP) or Cogeneration is primarily a thermal, technology neutral, energy efficient process. Input fuel could be biomass, coal, oil or natural/landfill gas. Technology could be steam turbine, gas turbine or reciprocating engine. The process allows us to simultaneously produce heat (steam) and electricity from a single fuel by making use of otherwise waste energy.



Efficiency= Useful
 Output/Input=80%

Consumption is usually 30%
 less with the same useful
 output energy when
 compared to that of stand-
 alone plant.

Combined Heat and Power

The benefits of CHP system are multi-fold. For example:

- CHP uses fossil fuels more efficiently, saving between 20% and 40% over stand-alone systems. In addition, CHP reduces energy costs by eliminating or deferring costly transmission and distribution infrastructure investments.
- CHP improves the reliability and security of energy supply by using local fuels and waste products as inputs. Many CHP facilities in Canada and in the US continued to supply power during the August 2003 blackout.
- CHP improves air quality, reduces the environmental impacts of energy use and produces less air pollutants than stand-alone alternatives.

CHP or cogeneration systems are classified according to the technology used to generate electricity. In this article, we will focus on steam turbine cogeneration because of our interest in its simplicity (the steam that drives the turbine is produced in a typical industrial boiler) and its flexibility (boilers are available that burn virtually any type of fuel). Furthermore, we would like to share with you the following:

- steam and steam turbine fundamentals;
- an example of a typical steam turbine cogeneration system to analyze steam turbine performance and the benefits that such system can bring; and
- another example to examine the conditions of eligibility for Canadian Capital Cost Allowance (CCA).

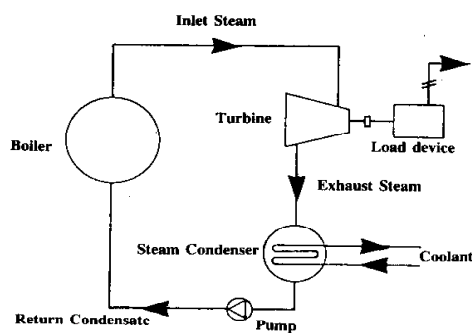
STEAM TURBINE TYPES

Steam turbines are classified by the conditions of the exhaust steam (see figures below).

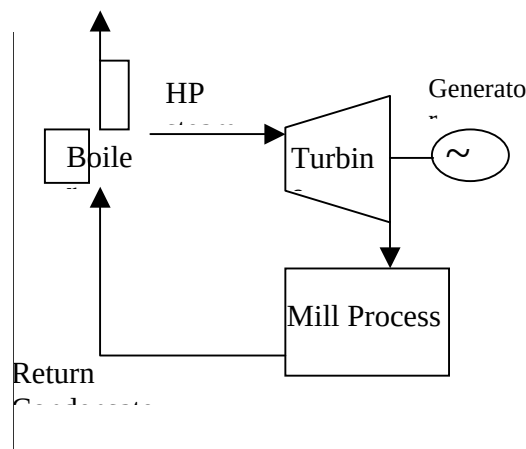
Condensing turbines usually utilize superheated inlet steam to minimize condensation within the turbine and operate the exhaust steam below atmospheric pressure.

Backpressure turbines operate with the exhaust steam at or above atmospheric pressure. They often utilize inlet steam at saturation pressure and temperature resulting in a mixture of steam and condensate at the exhaust.

Condensing



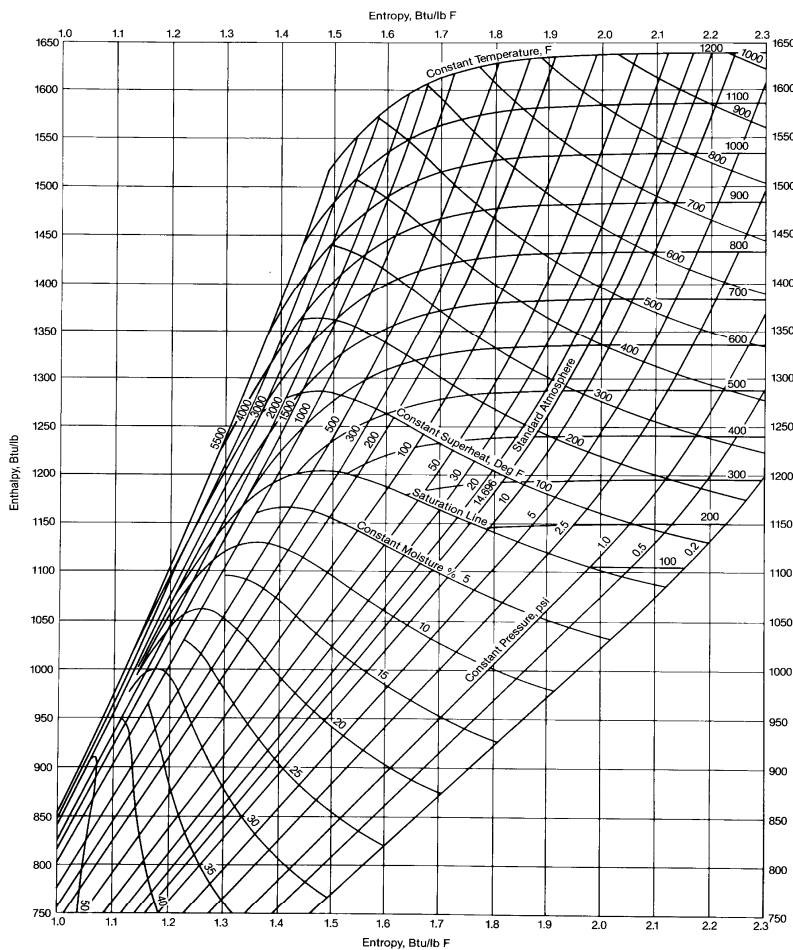
Non-condensing/backpressure



STEAM AND STEAM TURBINE FUNDAMENTALS

Here are some of the steam and steam turbine properties that are relevant in this article:

- Specific Enthalpy (h in Btu/lb of steam): is the amount of heat that a substance contains per unit mass.
- Entropy (s in Btu/lb F) is the rate of change of enthalpy per unit temperature change.
- Steam tables are tabulated listings of the following thermal properties of water and steam at various sustained temperatures and pressures.
 - The specific volume (ft^3/lb), for water at saturation temperature (v_f) and saturated steam (v_g).
 - The enthalpy for water at saturation temperature (h_f), evaporation or change of state (h_{fg}), and saturated steam (h_g).
 - The entropy for water at saturation temperature (s_f), evaporation or change of state (s_{fg}), and saturated steam (s_g).
- The values for saturated steam are for dry steam as pure vapour without entrained water droplets. The theoretical values can be used for most steam system calculations. Although most systems operate close to these theoretical values, some water is usually present. The amount of water is a measure of the steam “quality” and is expressed as “constant moisture per cent of weight”.



The Mollier Diagram (left) is a graphical representation of the steam table plotted with enthalpy on the vertical axis and entropy on the horizontal axis. Also included on the diagram are absolute pressures, temperatures, constant moistures percent and constant superheat temperatures. The major portions of the diagram are separated by the saturation line; below which, the steam contains some water droplets and above which, the steam is superheated and acts as a gas. (If superheating at constant pressure is continued the volume of the steam increases. Below the saturation line the temperature remains constant for a constant pressure.)

The Mollier diagram is used to determine characteristics of steam, usually from temperature and pressure information.

STEAM TURBINE PERFORMANCE

Manufacturers' performance information is the most reliable source of data for steam turbine operating characteristics. When the data is not available the energy consumption of a particular steam turbine can be estimated using measured data and the equations that are discussed here.

Ideal/Theoretical steam rate (ISR): It is the quantity of steam that will produce a unit of shaft energy output from an ideal steam turbine having no machinery or thermal loss.

$$\text{ISR (lb/kWh)} = 3413 / (h_i - h_o)$$

Where h_i : enthalpy of inlet steam (Btu/lb), h_o : enthalpy of outlet steam (Btu/lb), 3413: conversion of Btu to kWh

Actual steam rate (ASR): It is the flow of steam required to produce a particular shaft power output.

$$\text{ASR (lb/kWh)} = f_s / W_{to}$$

Where f_s : steam flow rate (lb/hr) and W_{to} : turbine shaft power output (kW)

Heat-to-Power Ratio: It is the ratio of the amount of useful thermal energy available to the amount of electricity generated and is usually expressed in Btu/kWh. For steam turbines, the Heat-to-Power ratios usually vary from 2:1 to 15:1.

Overall Steam Turbine Efficiency (Eff_t):

It is the ratio of the ideal steam rate to the actual steam rate, $\text{Eff}_t (\%) = \text{ISR}/\text{ASR} \times 100$

Energy extracted from steam to produce shaft energy

$$Q_e \text{ (Btu/hr)} = f_s \times (h_i - h_e)$$

h_i : enthalpy of inlet steam (Btu/lb), h_e : enthalpy of outlet steam and condensate at exhaust conditions (Btu/lb)

In many turbine applications the exhaust steam contains a significant amount of condensate. Sometimes, it is necessary to separately identify the energy content of the steam and the condensate in the equation for energy extraction.

$$\text{Thus, } Q_e = (f_s \times h_i) - (f_{co} \times h_{fo}) - ((f_s - f_{co}) \times h_{go})$$

f_{co} = exhaust condensate flow rate (lb/hr)

h_{fo} = enthalpy of outlet condensate (at the saturation temperature corresponding to exhaust steam pressure, h_f from steam table)

h_{go} = enthalpy of outlet steam (at the exhaust steam saturation pressure, h_g from the steam table)

Total energy required for a steam turbine system

$$Q_t \text{ (Btu/hr)} = f_s \times (h_i - h_r) \text{ where } Q_t: \text{ total steam system input, } h_r: \text{ enthalpy of return condensate (Btu/lb)}$$

Steam supply attributable to the operation of the turbine

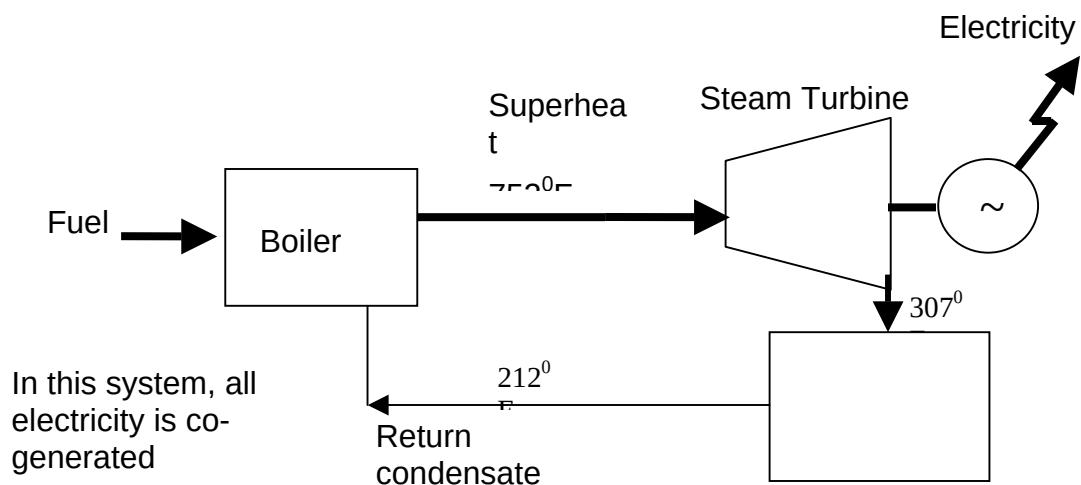
$$f_{st} = f_s \times Q_e / Q_t \text{ when all of the exhaust steam is condensed for other uses}$$

$$\text{Annual steam cost} = f_{st} \times t \times C_s$$

Where t = operation time (hr/yr) and C_s = unit steam cost (\$/lb)

STEAM TURBINE COGENERATION

An example is now carried out to illustrate the benefits of a typical steam turbine cogeneration. In it, a non-condensing turbine is used to drive a generator and reduces high pressure superheated steam to lower pressure saturated steam. The lower pressure steam is used for heating water and is condensed at 212°F. Please note that the lower pressure could be used for other purposes such as drying paper tissues.



Given:

Inlet steam pressure: 615 psi (absolute), inlet steam temperature: 752°F

Outlet steam pressure: 75 psi (absolute), outlet steam temperature: 307°F

Steam flow rate (measured): $f_s = 7289$ lb/hr, exhaust condensate flow rate (measured): $f_{co} = 218$ lb/hr

Unit steam cost, C_s : \$.01/lb, unit electrical cost, C_e : \$.08/kWh, operation time t : 8400 hr/yr

Turbine nameplate shaft power output, W_{ton} : 340 kW, turbine nameplate steam rate: 22 lb/kWh

Generator Efficiency, Eff_g : .92%, generator power output (measured): 309kW

Find:

Turbine efficiency, steam cost attributable to steam turbine, value of electricity generated and energy cost savings

Solution:

Shaft power input to generator: $309 \text{ kW} / .92 = 336 \text{ kW}$

Turbine connected to generator, drive loss negligible, turbine shaft power output, $W_{\text{to}} = 336 \text{ kW}$

To find ISR, use Mollier diagram/steam table/software, $h_i = 1378 \text{ Btu/lb}$, $h_o = 1182 \text{ Btu/lb}$

$\text{ISR} = 3413 / (1378 - 1182) = 3413 / 196 = 17.4 \text{ lb/kWh}$

$\text{ASR} = f_s / W_{\text{to}} = 7289 / 336 = 21.7 \text{ lb/kWh}$ (compared with the nameplate steam rate of 22 lb/kWh)

Overall steam turbine efficiency = $\text{ISR} / \text{ASR} = 17.4 / 21.7 \times 100 = 80\%$

$Q_t = f_s \times (h_i - h_r) = 7289 \times (1378 - 180) = 8.73 \times 10^6 \text{ Btu/hr}$ (h_r : the h_f column for 212°F condensate from steam table)

Energy extracted by the steam turbine

$Q_e = (f_s \times h_i) - (f_{\text{co}} \times h_{r,o}) - ((f_s - f_{\text{co}}) \times h_{g,o})$ (From steam table and the h_f and h_g column for 307°F steam)

$h_{r,o} = 277 \text{ Btu/lb}$, $h_{g,o} = 1182 \text{ Btu/lb}$

$Q_e = (7289 \times 1378) - (218 \times 277) - ((7289 - 218) \times 1182) = 1.63 \times 10^6 \text{ Btu/hr}$

Steam flow rate attributed to turbine: $f_{\text{st}} = f_s \times Q_e / Q_t = 7289 \times 1.63 / 8.73 = 1361 \text{ lb/hr}$

Annual steam cost of steam turbine = $f_{\text{st}} \times t \times C_s = 1361 \times 8400 \times 0.01 = \$114,324/\text{yr}$

Annual value of electricity = $W_{g,o} \times C_e \times t = 309 \times 0.08 \times 8400 = \$207,648/\text{yr}$

Annual energy cost savings = $\$207,648 - \$114,324 = \$93,324/\text{yr}$

CANADIAN CAPITAL COST ALLOWANCE (CCA) CLASS TAX 43.1

Under Class 43.1, eligible energy conservation property of qualifying systems can be written off at a 50% declining balance rate if the heat rate of the system is less than 6000 Btu/kWh. In general, qualifying systems are those that conserve energy by:

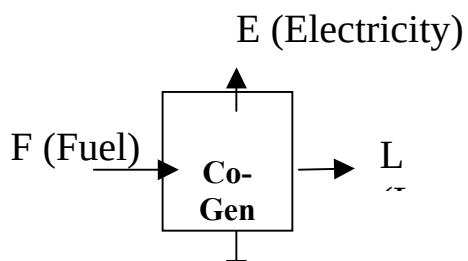
- Recovering and re-using thermal waste;
- Using specified-waste fuel;
- Using cogeneration; or
- Using renewable energy sources.

We will look at an example of natural gas fired steam turbine cogeneration, calculate the heat rate and determine the eligibility for CCA, tax class 43.1.

Doing an energy balance as illustrated below, we can determine the equations which can be used to calculate the heat rates:

Energy Balance, cont'd

Energy Balance



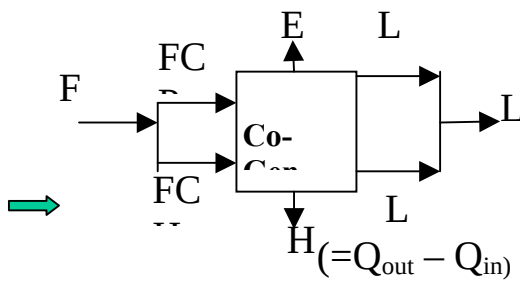
$$F = H + L + (E \times 3413)$$

F: Fuel, BTU/yr

H: Heat

L: Loss

E: Electricity



FCP: Fuel chargeable to electricity

FCH: Fuel chargeable to heat

L_E : Loss chargeable to electricity

L_H : Loss chargeable to heat

UHV Basic

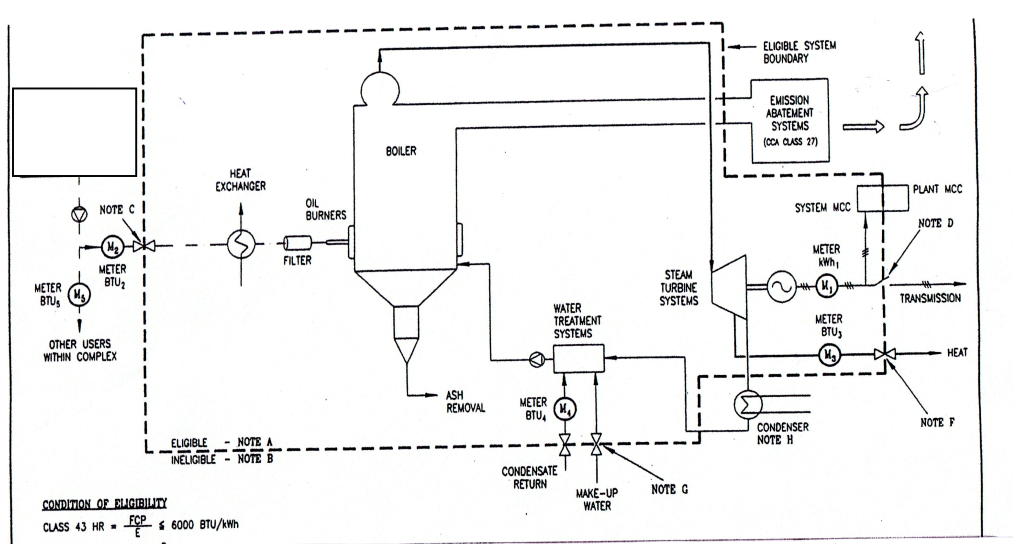
Therefore:

- $FCP = (E \times 3413) + L_E = F - H - L_H$, $L = F - (E \times 3413) - H = L_E + L_H$
- $L_E = L \times (E \times 3413) / (E \times 3413) + H$, $L_H = L \times H / (E \times 3413) + H$

Definition of Heat Rate = $FCP/E = F / (E + (H/3413))$

If it is ≤ 6000 Btu/kWh then the system is eligible under 43.1

Example, gas fired, steam turbine cogeneration system



Determine 43.1 Eligibility for the above co-gen system

Given: $M_1 = 543 \times 10^6 \text{ kWh}$, $M_2 = 4740 \times 10^9 \text{ Btu}$, $M_3 = 974 \times 10^9 \text{ Btu}$, $M_4 = 68 \times 10^9 \text{ Btu}$

Where M: meter

$E = 543 \times 10^6 \text{ kWh (M}_1\text{)}$, $H = M_3 - M_4 = 906 \times 10^9 \text{ Btu}$, $F = 4740 \times 10^9 \text{ Btu (M}_2\text{)}$

43.1 Eligibility = $F / (E + H/3413) = 4740 / 0.81 = 5852 \text{ Btu/kWh (Yes)}$

Or

$L = F - (E \times 3413) - H = 1981 \times 10^9 \text{ Btu}$, $L_H = L \times H / (E \times 3413) + H = 650 \times 10^9 \text{ Btu}$, $FCP = F - H - L_H = 3184 \times 10^9 \text{ Btu}$

43.1 Eligibility = $FCP/E = 3184/543 = 5860 \text{ Btu/kWh (Agreed with the previous answer with round-off)}$

CONCLUSION

Steam turbines are the most common cogeneration system used in industrial applications, particularly in the pulp and paper sector (because there is a significant amount of wood residue and other biomass available as input fuel) and some in the oil sand sector with steam coming from boilers burning petroleum coke. Steam turbines are very flexible because the steam that drives the turbine is produced in a typical industrial boiler which is easily modified to burn virtually any type of fuel, including waste fuels such as pulping liquor, landfill gas, forest residue and other biomass. Steam turbine system is robust because there are very few moving parts and is easy to maintain. As we have seen previously, steam turbine performance analysis is straightforward to carry out with very simple tools.

Steam turbine cogeneration systems usually produce significantly more heat than electricity per unit of fuel consumed and therefore have high heat-to-power ratios. Steam turbines come in two types, back-pressure turbines and condensing turbines. Back-pressure turbine is used when the exhaust steam is needed for other processes such as drying papers or heating water and condensing turbine is employed when the operator wants to maximize the work done by the turbine such as producing more electricity. Therefore, when selecting the turbine type during the design stage, the operator needs to consider the future duty performed by the turbine carefully.

It is estimated that the existing CHP in Canada is responsible for a reduction of at least 15Mt of GHG emissions and significant reduction in other air pollutants as well if the electricity produced by cogeneration were produced by stand-alone plants. As mentioned earlier, CHP has other benefits including increasing electricity supply security and reducing energy

costs through increased efficiency. It is for these same benefits that the European Union (EU) has encouraged its member states to double the amount of CHP by 2010, from 9% of total electric capacity to 18% (EU Commission 1997). In the US, government agencies and industry groups have been trying to double CHP by the same year from 55 GW to 110 GW (US CHP Association 2001).

In its 2005 budget, the Canadian federal government signaled its intention to encourage more CHP by increasing the CCA tax deduction from 30% to 50% on a declining balance basis. In addition to the attractive CCA rate, the payback period for implementing a steam turbine cogeneration project might be as short as 3 years depending on the difference between the local steam and electricity price. As market penetration of CHP in Canada is much smaller compared to that of the EU and the price of fossil energy has stayed very high (US\$85-\$90/barrel of oil) in 2007-2008, there is a lot of opportunity to implement CHP in Canada. The more successful CHP projects we have, the more benefits everyone (stakeholder, the community, the government and the environment) will gain.

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