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ASSESSMENT OF MID TEMPERATURE SORBENT DESULFURISATION TECHNOLOGY IN PUERTOLLANO IGCC PROCESS (Task 1)

-Description of the technology-

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Executive Summary

Hot-Gas Desulfurization (HGD) of raw-syngas in integrated gasification combined cycle (IGCC) power systems has received a great deal of attention over the past three decades due to the potential for high thermal efficiency (up to 50 %) and low environmental impact of these advanced power systems using HGD. The HGD is attractive since it is expected to improve the thermodynamic performance of the power plant, as well as simplifying the plant configuration, potentially reducing the investment costs. Higher efficiency and lower cost are achieved by efficient integration of modular designs of the gasification, hot-gas cleanup, and turbine subsystems. For this purpose, great efforts are now underway to develop dry gas purification technology that purifies hot coal gasification gas as it is. Mid temperature desulfurization is achieved by the use of a solid sorbents such as oxides of those metals that form stable sulfides, based on the non-catalytic reaction between a metal oxide and hydrogen sulfide. The optimum desulfurization temperature has been recommended in the range of 300 to 450 °C, also in according to the more favourable thermodynamic equilibrium of sulfur compounds removal. In addition, the sorbent must be stable in the coal gas atmosphere, have acceptable sulfur loading capacity, be regenerable, and maintain activity through a large number of sulphidation/regeneration cycles for its commercialization. All these properties could not be met by a single metal oxide. For this reason metal oxides are tried in combinations in the hope to improve thermodynamic, kinetic, and physical properties. Sorbents based on zinc oxide, currently the leading candidates, can effectively reduce the H_2S in coal gas to around 10 ppm levels and can be regenerated for multicycle process. The development of Hot Gas Clean-Up (HGCU) systems for acid gas and particulates removal from syngas has been pursued in the *U.S.*, *Europe*, and *Japan* and *Korea* since the 1970s. Various HGCU systems have been tested at the pilot plant level and a small number have been installed in commercial-scale IGCC demonstration plants:

- *Japan*, Ishikawajima-Harima Heavy Industries Co., Ltd. built a fluidized-bed desulfurization at Nakoso IGCC pilot plant (200-ton/day) with a coal gas production of 4360 and Kawasaki Heavy Industries, Ltd. (with a moving bed reactor) and Mitsubishi Heavy Industries, Ltd. developed an iron oxide-based honeycomb desulfurization agent treating 1090 Nm^3/h of coal gas.
- *U.S.A.*, RTI International and Eastman Chemical Company developed a new high-pressure dual-loop transport reactor design for HGCU, operated for more than 3,000 hours with an

effluent syngas sulfur concentration consistently <10 ppmv (~99.9% sulfur removal efficiency), with <5 ppmv sulfur being consistently achieved at optimal operating conditions. In October 2011 has presented its proposed project to demonstrate the pre-commercial scale-up of RTI's high-temperature syngas cleanup and carbon capture and sequestration technologies.

- 260 MW coal-fired IGCC at Tampa Electric Company's (TECO's) Polk County Station in Florida, equipped with both a 100% capacity CGCU (Cold Gas Clean-Up) system and a 10% capacity HGCU system based on a down-flow moving-bed H_2S adsorption process.
- Piñon Pine IGCC system in Nevada, designed with a KBR air-blown, fluidized-bed gasifier with limestone injection for partial in-situ H_2S capture (as CaS).

The development of hot gas clean-up systems for deep cleaning of sulfur from syngas appear to be long-term prospects, if at all achievable. Large scale demonstrations have not been achievable or practical before 2010. Justification for such demonstrations could become difficult if commercial IGCC projects with CGCU continue to proliferate and operate well over the next several years.

Objective

This intermediate report represents the first part of the project *"Assessment of mid-temperature sorbent desulfurization technology in Puertollano IGCC process"*. It covers the fundamentals, status, and future developments of sorbent materials and their application in the gas-solid adsorptive separation of the sulfur compounds from syngas.

The objective of this work is to gather information to provide an overview on hot gas cleanup for performing a comprehensive assessment of hot gas cleanup systems for advanced IGCC. As the status of hot gas cleanup is continually changing, additional current data are being obtained for this work up to 2011.

General basic principles of "sorbent technology"

A sorbent is usually a solid substance that adsorbs or absorbs another type of substance. It is the sorbent that makes a sorption process a unique and different separation and purification process from others. With the rapid development in novel sorbent materials and innovative cyclic adsorption processes, sorption has become a key separation process in many process industries including chemical, petrochemical, environmental, pharmaceutical, and electronic gases.

Adsorption mechanism and sorbent materials:

According to King, a mass separating agent is needed to facilitate separation form any separation processes [1]. The mass separating agent for adsorption process is the adsorbent, or the sorbent. Therefore, the characteristic of the sorbent directly decides the performance of any adsorptive separation or purification process. The basic definitions of adsorption-related terminologies are given in the following to clarify and standardize these widely used terms in this field.

- *Adsorption*: The adhesion of molecules (as of gases, solutes, or liquids) to the surfaces of solid bodies or liquids with which they are in contact.
- *Absorption*: The absorbing of molecules (as of gases, solutes, or liquids) into the solid bodies or liquids with which they are in contact.
- *Sorption*: Formation from adsorption and absorption.
- *Adsorbent*: A usually solid substance that adsorbs another substance on its surface.
- *Sorbent*: A usually solid substance that adsorbs and absorbs another substance.
- *Adsorbate*: Molecules (as of gases, solutes, or liquids) that are adsorbed on adsorbent surfaces.
- *Microporous*: Pore size smaller than 20 Å.
- *Mesoporous*: Pore size between 20 and 500 Å.
- *Macroporous*: Pore size larger than 500 Å.

Adsorptive separation can be achieved through one of the following mechanisms. Understanding the fundamentals of adsorptive separation mechanisms will allow to better design or modify sorbent materials to achieve their best possible separation performance [2–4].

Adsorption equilibrium effect is because of the difference in the thermodynamic equilibria for each adsorbate/adsorbent interaction. The majority of adsorptive separation and purification processes are based on equilibrium effect.

Adsorption kinetics effect arises because of the difference of rates at which different adsorbate molecules travel into the internal structure of the adsorbent. There are only a few commercial successes using adsorption kinetic difference to achieve adsorptive separation of gases.

Molecular sieving effect, also called steric effect, is derived from the molecular sieving properties of some adsorbents with a microporous structure. In this case, the pore openings of the adsorbent structure are small enough to exclude large adsorbate molecules from penetrating the micropores of the adsorbent. This is the extreme case of the kinetic effect. There are several commercial applications based on this mechanism in adsorptive separation processes. One typical example is separating normal paraffin from iso-paraffin and aromatics in an adsorption process using zeolite 5A as an adsorbent. n-Paraffin, with a long straight chain, has a smaller effective diameter than the well-defined aperture of zeolite 5A. Therefore it adsorbs in the micropores of the adsorbent during the adsorption step, and is recovered from the adsorbed phase in the desorption step.

General characteristics of sorbent materials:

Commercial sorbents used in cyclic adsorption processes should ideally meet the following requirements:

- Large selectivity derived from equilibrium, kinetic, or steric effect;
- Large adsorption capacity;
- Fast adsorption kinetics;
- Easily regenerable;
- Good mechanical strength;
- Low cost.

The above adsorbent performance requirements can simply transfer to adsorbent characteristic requirements as follows:

- Large internal pore volume;
- Large internal surface area;
- Controlled surface properties through selected functional groups;
- Controlled pore size distribution, preferably in micropore range;
- Weak interactions between adsorbate and adsorbent (mostly on physical sorbents);
- Inorganic or ceramic materials to enhance chemical and mechanical stability;
- Low-cost raw materials.

These basic requirements are usually proposed for adsorbents used in cyclic adsorption processes that are based on physical adsorption. There is an increasing demand for strong chemical adsorbents used in purification processes to remove trace contaminants from main stream fluids such as the removal of very toxic contaminants from electronic process gas streams, and the removal of toxic, or radioactive species from contaminated water. In these cases, the sorbents are used as "getter" materials. So, another very important mechanism in chemical adsorptive separation is the *"gas-solid reaction"* where a solid reacts more or less readily with reactive gas species with a reaction mechanism dependent both of physical diffusion (external and internal) and chemical reaction (toward the over-all mass transfer rate). Commercial sorbents that have been used in large-scale adsorptive separation and purification processes include activated carbon, zeolites, activated alumina, silica gel, and polymeric adsorbents. Although the worldwide sales of sorbent materials are relatively small as compared with other chemical commodities, sorbents and adsorption processes play a very important role in many industrial process. The estimated worldwide sales of these sorbents are as follows [2]:

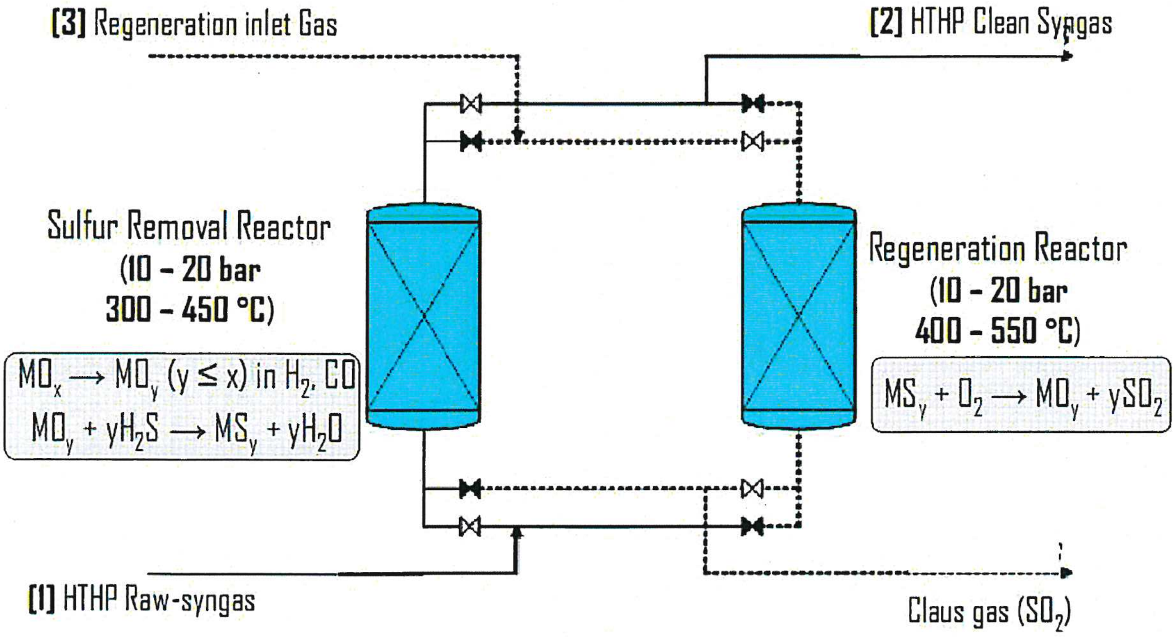
- Activated carbon: $1 billion;
- Zeolite: $1.07 billion;
- Activated alumina: $63 million;
- Silica gel: $71 million;
- Polymeric adsorbents: $50 million.

New developments in sorbent materials and applications:

The past two decades have witnessed major advances in new nanostructured sorbent materials including mesoporous molecular sieves, sol–gel-derived metal oxide xerogels and aerogels, metal organic framework, composite adsorbents, new carbonaceous materials (carbon nanotubes, carbon fibers, superactivated carbons), high-temperature ceramic sorbents, and strong chemical sorbent materials. Although these new sorbent materials have demonstrated promising sorption properties for many existing and new applications, systematic studies on synthesis methods and characterization of these new materials are necessary to fully explore and realize their potential as commercial sorbents.

Features of the technology

Integrated Gasification Combined Cycle (IGCC) technology is receiving increased attention because of its promise of higher thermal efficiency and reduced environmental impacts compared to today's coal fired plants. Current IGCC plants operate with an efficiency of about 43%, compared to 35% for a conventional coal plant. With improved gas turbines and high temperature gas cleanup technology, efficiencies exceeding 52% by the end of 2010 and 60% by year 2020 are targeted [5]. In a coal gasifier, unlike coal combustion processes, the sulfur in the coal is released in the form of hydrogen sulfide, H_2S, rather than sulfur dioxide (SO_2). The IGCC process must employ hot gas cleanup techniques to remove sulfur and other impurities in the fuel gas stream, principally to meet the stringent governmental regulations for sulfur emissions and also to protect turbine components from the corrosive action of H_2S [6]. Typical gasifier exhaust contains about 5000 ppmv H_2S whereas sulfur concentration limitation of approximately 150 ppmv for IGCC systems has been established. Therefore, a desulfurization system capable of reducing H_2S concentration from about 5000 ppmv to 150 ppmv or lower is required [7]. Hydrogen sulfide should be removed from the product gas while it is still hot so that the gas can be used directly without losing its heat. This completely eliminates the costly, less efficient method of low temperature, liquid based, fuel gas scrubbing systems. Additionally, since the volume of the fuel gas stream is a lot similar than that of the flue gas stream, the removal of H_2S at high temperature results in considerably lower hardware costs than would be required by a conventional SO_2 scrubbing method at low temperature [6]. This fact emphasizes the importance of "hot gas cleanup". Desulfurization by adsorption (ADS) is based on the ability of the solid sorbent to selectively adsorb sulfur compound from gas streams. ADS is divided in two groups: *"Adsorptive desulfurization"* and *"Reactive adsorption desulfurization"*. Adsorptive desulfurization is based on physical adsorption of sulfur compounds on a solid sorbent surface. Regeneration of the sorbent is usually done by flushing the spent sorbent with a desorbent, resulting in a high sulfur compound concentration flow. Reactive adsorption desulfurization is based on chemical interaction of the sulfur compounds and the sorbent. Sulfur is "fixed" in the sorbent, usually as sulfide, and the S-free hydrocarbon is released into the purified fuel stream. Regeneration of the spent sorbent results in sulfur elimination as H_2S, S, or SO_x depending on the applied process. Efficiency of desulfurization is mainly determined by the sorbent properties: its adsorption capacity, selectivity for the sulfur compounds, durability and regenerability [8]. The high temperature desulfurization can be successfully accomplished by using metal oxide sorbents which will react with H_2S to form the corresponding metal sulfide and which, according to thermodynamics, have the ability to reduce the H_2S concentration to the required level. In addition, the sorbent must be stable in the coal gas atmosphere, have acceptable sulfur loading capacity, be regenerable, and maintain activity through a large number of sulphidation/regeneration cycles [9]. All these properties could not be met by a single metal oxide. For this reason metal oxides are tried in combinations in the hope to improve thermodynamic, kinetic, and physical properties. A simple representation of the desulfurization/regeneration solid sorbents technology, following the concept of two fluidized bed reactors is shown on Fig. 1.



[1] (% v/v) CO (61.25), H_2 (22.33), CO2 (3.70), N_2 (10.5), Ar (1.02), H_2S (1.01), COS (0.17), CH_4 (0.01)
[2] (% v/v) CO (61.25), H_2 (22.33), CO_2 (3.70), N_2 (10.5), Ar (1.02), S compounds (ppm levels), CH_4 (0.01), H_2O
[3] Air + N_2 variable for different level of O_2 or evaluate to use steam

Fig.1 : Schematic representation of the desulfurization/regeneration solid sorbents technology

Current Acid Gas Removal (AGR)

Currently, the processes of choice in commercial IGCC facilities for the removal of acid gases are both the chemical solvent AGR processes based on aqueous methyldiethanolamine (MDEA) and the physical solvent-based Selexol process which uses mixtures of dimethyl ethers of polyethylene glycol [10]. In most of the IGCC applications now, with both of these AGR processes, the AGR units are preceded by carbonyl sulfide (COS) hydrolysis units to convert most of the COS to H_2S. This then enables the AGR units to accomplish deeper total sulfur removal and lower H_2S

levels. Total sulfur (COS + H_2S) levels of <20 ppmv may be required if selective catalytic reduction (SCR) is to be used with IGCC to prevent ammonium sulfate salt deposition and corrosion problems in the colder sections of the heat recovery steam generator (HRSG). While physical solvent processes are capable of meeting the stringent sulfur cleanup required for SCR, the processes themselves are more expensive than the MDEA-based amine ones. With COS hydrolysis, MDEA-based solvents can also meet a 10-20 ppmv total sulfur level in the treated gas, albeit at the expense of increased solvent circulation rates and a decrease in H_2S selectivity. The use of MDEA-based solvents will require acid gas enrichment (AGE) to give a suitable feed for the Claus plant. Commercial MDEA formulations (with proprietary additives) have been developed, which offer enhanced selectivity for H_2S, and their use is widespread in the gas treating industry. BASF Corporation has shown some success in tests of its newly formulated MDEA solvent that removes much of the COS while retaining a high degree of H_2S selectivity. However, the performance to date is not adequate for the elimination of the COS hydrolysis step. SFA Pacific believes that if SCR is to be used, COS hydrolysis will be necessary for any acid gas removal system, except possibly the Rectisol process. Although the Selexol process by itself is more expensive than an MDEA AGR process, the total AGR, sulfur recovery (SR) process, and tail gas treating (TGT) process package based on Selexol could be more cost effective than the package based on MDEA especially if the syngas pressure is high and deep sulfur removal is required (i.e., to 10-20 ppmv). Deeper desulfurization can be accomplished by chilling the Selexol process. However, CO_2 co-absorption then also increases. For future IGCC with CO_2 removal for sequestration, a two-stage Selexol process presently appears to be the preferred AGR process as indicated by ongoing engineering studies at EPRI and various engineering firms with IGCC interests. In CO_2 removal applications, the Selexol process is chilled thus facilitating deep H_2S removal as well as CO_2 removal. The Rectisol physical solvent AGR process based on low-temperature (refrigerated) methanol is capable of deep total sulfur removal, but it is regarded as the most expensive AGR process. Therefore, its use is generally reserved for chemical synthesis gas applications in which very pure syngas is required. Its use in IGCCs with CO_2 removal has also been proposed. Further studies of the main IGCC processes with various feedstocks and all of the potentially competitive AGR options are required to quantify the relative performance and cost benefits of the various options and elucidate the ranges of conditions and cases in which they are competitive. Related studies are underway at EPRI and various engineering organizations.

New Hot Gas Desulfurization technology:

High- and mid- temperature desulfurization of coal derived fuel gas from the coal gasification unit is considered as one of the most promising advanced technologies to remove the sulfur components from coal so that environmental considerations are eliminated from the choice of using coal versus oil or natural gas as fuel feedstock. In addition, the method offers potential improvements on the thermal efficiency of the systems using coal gasification, such as integrated gasification combined cycle (IGCC) power plants, hydrogen fuelled solid oxide fuel cells (SOFC) and molten carbonate fuel cells (MCFC) technologies. The development of these systems depends on the ability to remove sulfur compounds, mainly H_2S, from the coal gas.

The important factors of hot gas desulfurization sorbent are:

1. The sorbent should have good sulfur removal capacity and fast adsorption kinetics;
2. The sorbent should be chemically stable, i.e., it should not evaporate or sinter during regeneration;
3. The sorbent should be physically stable, i.e., it should withstand any attrition;
4. The sorbent should catalyze formation of elemental sulfur upon reductive regeneration, hydrolyze carbonyl sulfide (COS), and react with other contaminants such as tars;
5. The sorbent should be regenerable and it should maintain its sulfur removal capacity for many cycles;
6. The sorbent replacement cost should be affordable.

Process requirements taken as a basis for determining metal oxides suitability for high- mid-temperature desulfurization:

1. Rate of desulfurization and stability of the sulfide under reducing gas conditions;
2. Potential for detrimental secondary reactions on the solid under reducing coal gases (e.g. metal carbides, reduction to zero-oxidation state, formation of chlorides from HCl);
3. Rate of regeneration and production of SO_2 or elemental sulfur under oxidizing gas conditions;
4. Potential for detrimental secondary reactions on the solid under oxidizing gases (e.g. sulfates) and hydrothermal stability during regeneration.

The chemistry of a complete sulfidation-regeneration cycle may be represented by the overall reactions:

<u>Reduction</u>: $MO_x \rightarrow MO_y$ ($y \leq x$) in H_2, CO

<u>Sulfidation</u>: $MO_y + yH_2S \rightarrow MS_y + yH_2O$

<u>Regeneration</u>: $MS_y + O_2 \rightarrow MO_y + ySO_2$

<u>Historical Development of Regenerable Desulfurization Sorbents</u>

Over the last two decades a number of studies have been reported on high-temperature H_2S removal, primarily using various transition metal oxides as regenerable sorbents. The sorbent most intensively studied in the 1980's was iron oxide, which yields equilibrium H_2S concentrations in the few hundred ppm range for a composition representative of low-Btu coal derived gas and temperatures of above 500 °C. While the sulfidation kinetics of iron oxide are very good, this sorbent cannot be used for single-stage coal gas desulfurization to reduce the H_2S content of the fuel gas down to a few ppm of sulphur [11]. Zinc oxide has been used as a non-regenerable sorbent in "guard beds" protecting catalyst beds from trace sulfur impurities. More recently, zinc oxide has also been investigated as a regenerable sorbent. The thermodynamic equilibrium for sulfidation of ZnO is quite favorable, yielding desulfurization down to a few ppm H_2S. The sulfidation kinetics of ZnO, however, are slower compared to those of pure iron oxide, and the regenerability of ZnO is restricted above 700 °C by the loss of surface area and the formation of zinc sulfate at low regeneration temperatures.

In the late 1980's, it was shown that certain mixed oxides have superior properties compared to single oxides for hot gas cleanup. Many investigators have been conducting research to develop a superior mixed metal oxide sorbent. Mixed-metal oxide sorbents have been studied in the past both as straight zinc titanates, (e.g., Zn_2TiO_4 and $Zn_2Ti_3O_8$) or as combinations of oxides of vanadium, copper, manganese, cobalt, and others. Although zinc titanate has also shown better attrition resistance than zinc ferrite in pilot tests, this sorbent also suffers gradual loss of reactivity in long-term cyclic operation, resulting in high fresh sorbent makeup rate to maintain the desired level of desulfurization [11].

Other mixed metal oxides such as copper-based and cobalt-based sorbents have also been investigated; however, the research has been limited to laboratory-scale equipment. Although higher temperature application offers better overall process efficiency, the stringent requirement for sulfur removal efficiency at temperatures above 538 °C limits the choice of the sorbents to a few metal oxides (based on thermodynamic equilibrium). The thermodynamic equilibria of many metal oxides significantly improve as the temperature decreases, making many metal oxide sorbents suitable for hot gas cleanup application in the temperature range of 343-538 °C. Although the initial chemical reactivities of the sorbents generally decrease with decreasing temperature, the lower thermal stress incurred can lead to better sorbent reactivity after a large number of cycles, reducing the sorbent replacement cost. In general, the benefit to be gained by lower temperature application may outweigh the slight loss of efficiency, resulting in lower overall cost of electricity. However, no extensive study has been done on the development of advanced sorbents for the lower temperature application.

Properties of Metal Oxide Sorbents for Hot Gas Desulfurization

A good sorbent will allow for a deep desulfurization to ppm levels and have good regeneration properties. This means the combination of a high affinity towards the reaction with H_2S, as well as the formation of a sulphide which can be converted back to the oxide through oxidation with air or diluted air. Next to the residual H_2S level, sorbent durability is the critical issue. For economical operation, a good sorbent has to maintain a large fraction of its desulphurisation properties for a large number of sulfidation-regeneration cycles, requiring excellent sorbent stability.

As summary, in order for a metal oxide to be considered suitable for high-temperature desulfurization, the material must exhibit desirable properties in the following areas:

- Ability to remove reduced sulfur compounds such as hydrogen sulphide and carbonyl sulfide to less than 100 ppmv;
- Good sulfur loading capacity to reduce the operational cost and reactor size;
- Good regenerability;
- Mechanical strength measured as either crush strength or attrition resistance;
- Retaining its capacity over an extended period of time without undergoing drastic changes in its physical and chemical properties in order to minimize frequent replenishments;
- Environmental affinity.

Selection of Metal Oxide Sorbents for Hot Gas Desulfurization

Westmoreland and Harrison (1976)[12] screened the high-temperature desulfurization potential of twenty-eight (28) solids, primarily metal oxides. They concluded that eleven candidate solids based upon the metals Fe, Zn, Mo, Mn, V, Ca, Sr, Ba, Co, Cu, and W showed thermodynamic feasibility for high-temperature desulfurization. They also determined the initial rates for the reaction between H_2S and MnO, CaO, ZnO, and V_2O_3 over a temperature range of 300 to 800 °C, in a thermobalance reactor. The relative magnitude of reaction rates decreased in the order MnO > CaO ≈ ZnO > V_2O_3. They concluded that MnO possessed favourable properties for a high-temperature desulfurization process and highly recommended that further studies be carried out. Fractional desulfurization results are summarized in Fig. 2. From figure 2, it is obvious that manganese, for example, satisfies the 95% desulfurization criterion at all temperatures below 1060 °C. Figure 3 summarizes solid stability results. As an example, consider barium. At low temperature, $BaCO_3$ is the stable solid form. Sulfiding of the carbonate begins at approximately 800 °C, and, from that point to the 1200 °C melting temperature of BaS, simultaneous existance of solids BaS and $BaCO_3$ is predicted.

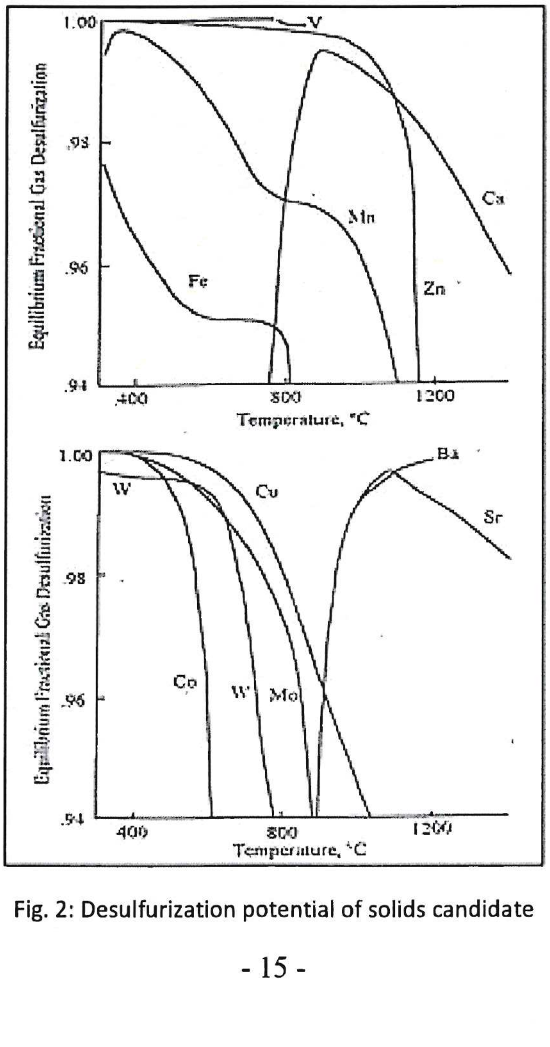


Fig. 2: Desulfurization potential of solids candidate

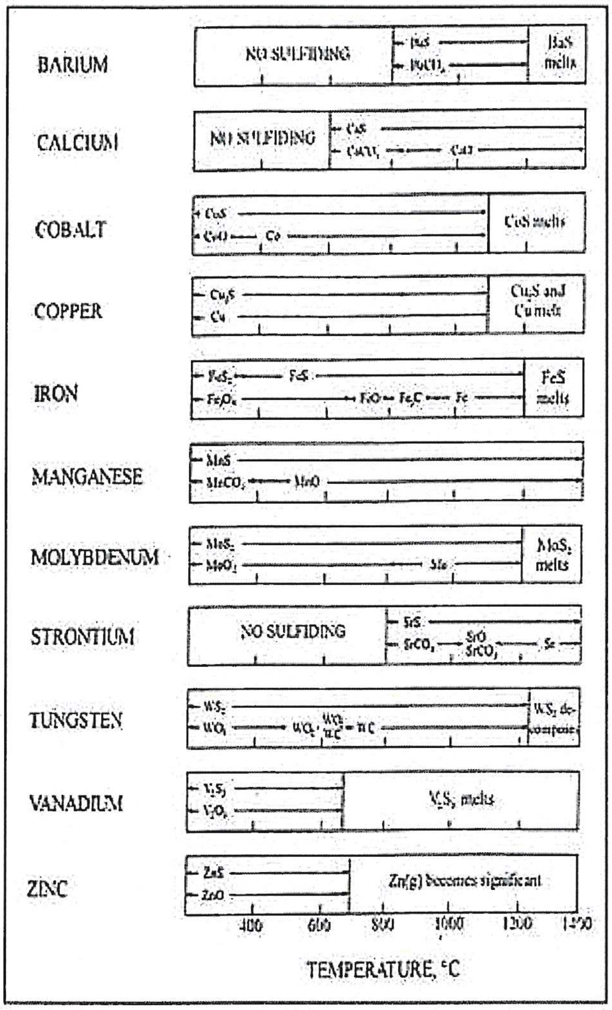


Fig. 3: Stable solid phases of solids candidate

By properly combining information from Figures 2 and 3, the desulfurization potential of several canditate can be established. These results are summarized in the following paragraphs.

Cobalt: Cobalt satisfies desulfurization criterion to a maximum temperature of 600 °C with CoS the sulfided product. In the reducing atmosphere of coal gas, excess cobalt would be present as the metal at temperatures in excess of 300 °C.

Copper: The behaviour of copper and cobalt is similar, although copper maintains 95% desulfurization capability to a temperature in excess of 900 °C. In the reducing atmosphere, excess copper would be present in metallic form over the entire temperature range.

Iron: Iron is a suitable desulfurizing material at temperatures up to 700 °C. At these temperatures, Fe_3O_4 is the stable form of excess iron. The rapid decrease in fractional desulfurization near 700 °C corresponds to Fe_3O_4 reduction to FeO.

Manganese: Oxide stability and high fractional desulfurization are predicted to temperatures in excess of 1000 °C. Below 400 °C, MnO is stable. Importantly, manganese shows desulfurization potential in the temperature range of 600-700 °C where metal oxides currently known to be reactive with H_2S are unsatisfactory.

Vanadium: In the reducing atmosphere, V_2O_3 is the stable form of the excess metal. Essentially 100% desulfurization, with V_2S_3 as the sulfided product, is predicted up to the melting temperature of V_2S_3 near 650 °C.

Zinc: On the basis of fractional desulfurization, zinc is acceptable to 1150 °C with ZnS as the sulfided form and ZnO as the stable form of excess zinc. However, zinc is limited to a maximum temperature of approximately 700 °C because of the formation of zinc vapour. Experimental observations in this laboratory have confirmed the formation of zinc vapour in similar atmospheres at temperatures in excess of 700 °C.

From the initial screening of metals, the following metals should be ruled out immediately: Ba, Ca, Sr, and V. The main reason was the lack of sulfidation of their oxide forms in the desired range of 340-550 °C or incompatibility with turbine operation (i.e., high-temperature corrosion by vanadium compounds). The process of selection of metal oxides for desulfurization identified the following metals as being potentially useful for desulfurization study: Zn, Cu, Co, Fe, Ce, Mo, Mn, Sn, W, Ni. It was agreed that many of these metals have weaknesses when considered as pure metal oxides, but become useful when used in combination with others (e.g., Cu-Mo, and Zn-Mo systems). Zn, Cu, Fe, Ce, and Mo were ranked as being the most useful, hence worth further evaluation. Both molybdenum and tungsten oxides have good desulfurization potential; however, they are temperature limited because of possible carbide formation [13]. More information on thermodynamic properties is needed on the W system to proceed forward with an evaluation. Cobalt exhibits similar behaviour to that of copper in its tendency to reduce to the metallic form in fuel gas atmospheres. However, compared to copper oxide, desulfurization with cobalt oxide is more temperature limited and becomes less efficient with increasing temperature. In addition, cobalt sulfide requires significantly higher temperatures for regeneration than copper sulphide [14]. Sn and Ni were ranked as being less desirable than the others and probably will not be considered before the others. Sn has one of the highest H_2S vapor pressures and its sintering temperatures are relatively low, which may affect the regeneration process conditions, typically done from 500 to 700 °C.

The next step was consideration of the relative compositions in formulations. The metals still considered as useful at that point were divided into three functional groups:

1. Main components for desulfurization;
2. Secondary components for desulfurization, chemical stability, or porosity modifier;
3. Structural component to maintain mechanical durability.

Up to this point, the selection of metal oxides is a general method that is equally applicable to any desulfurization process configuration operating in the prescribed temperature regime.

Zn, Fe, Ce, Mn and Cu were selected to be the next generation of most promising metals for use as main components. Secondary components will be added to the main components to satisfy most of the evaluation criteria and a structural component will be needed to maintain morphological and mechanical durability. All these properties could not be met by a single metal oxide. For this reason metal oxides are tried in combinations in the hope to improve thermodynamic, kinetic, and physical properties. By mixing, it may be possible to:

1. improve sulfur removal efficiency;
2. prevent or slow the reduction to elemental metal;
3. prevent sulfate formation;
4. improve dispersion and modify porosity and pore size;
5. impart structural strength and stability [15].

The stability of the sorbent is an important property as the sorbent should withstand highly reducible atmospheres and high temperature range of 400-800 °C without reducing into elemental metal form or vaporize [12, 15]. Another sorbent property is sulfur loading capacity or sulfur adsorption capacity which is defined as the ratio of sulfur adsorbed to initial sorbent by weight [16].

$$\textbf{\textit{Sulfur Loading Capacity}} = \frac{\textit{theoretical amount of sulfur adsorber by the sorbent }(g)}{\textit{total weight of sorbent }(g)}$$

The conversion of H_2S and the selectivity to sulfur are defined as follows:

$$\textbf{Conversion of } H_2S\ \textbf{(\%)} = \frac{[H_2S]_{inlet} - [H_2S]_{outlet}}{[H_2S]_{inlet}} * 100$$

$$\textbf{Selectivity to sulfur (\%)} = \frac{[H_2S]_{inlet} - [H_2S]_{outlet} - [SO_2]_{outlet}}{[H_2S]_{inlet} - [H_2S]_{outlet}} * 100$$

where:

$[H_2S]_{inlet}$: inlet H_2S concentration

$[H_2S]_{outlet}$: outlet H_2S concentration

$[SO_2]_{outlet}$: outlet SO_2 concentration

The cost of purchasing raw materials was also considered in the evaluation of the relative merit of the various metal oxides. Costs were kept in mind when developing formulations, but it was considered too early to make decisions whether to use or not to use an oxide just because of its price, since the relative amounts of secondary components may be too small (e.g., <1%) to have a significant impact on the cost of the sorbent and yet have a tremendous impact on the durability of the material.

Sorbent Regeneration

Regeneration is considered essential to the commercialization of sulfur sorbents since it improves overall process economics and also reduces the amount of solid waste generated and ultimately landfilled. The regeneration step is a highly exothermic oxidation process requiring careful temperature control. Too high temperature (above 800 °C) sinters and destroys the sorbent structure and reduces its ability to absorb sulfur in consecutive absorption steps. Low temperature, high SO_2 and O_2 result in sulfate formation and a lower sulfur removal efficiency [17]. Metal sulfides are regenerated to oxides and by-product SO_2 containing stream by steam, oxygen or SO_2 gases.

$$MeS + H_2O \rightarrow MeO + H_2S$$

$$xMeS + (y/2)SO_2 \rightarrow Me_xO_y + (x+y/2)S$$

$$xMeS + (x+y/2)\ O_2 \rightarrow Me_xO_y + xSO_2$$

An unwanted side-reaction is the formation of sulphates:

$$MeS + O_2 \rightarrow MeSO_4$$

Because the formed sulphate is inert with respect to the desulphurisation and thus there is a loss of active material. Consequently, it is important to know at which conditions this reaction precedes the desired regeneration reaction. For the process to be economical, the sorbent must be regenerable and must maintain activity through many sulfidation-regeneration cycles. Most regeneration studies to date have used total oxidation in which the metal sulfide is reacted with oxygen to regenerate the metal oxide and liberate the sulfur as SO_2. In addition to the problem of controlling SO_2 in the regenerator off-gas, the highly exothermic total oxidation reaction creates reactor temperature control problems which may accelerate the deteriorating of the high surface area, porous sorbent. Decreasing the oxygen concentration of the regeneration gas to assist in temperature control reduces the SO_2 concentration in the regeneration product and complicates the SO_2 control. Direct production of elemental sulfur during sorbent regeneration would alleviate both problems. Elemental sulfur is a marketable by-product which can be separated by condensation and safely stored and transported. Three possible elemental sulfur production concepts were identified from the literature. The general chemistry of each as well as a brief summary of the literature is presented below.

Reaction With SO_2

The generic reaction between metal sulfide and SO_2 to yield elemental sulfur is:

$$MeS_{(s)} + 0.5\ SO_{2\,(g)} \rightarrow MeO_{(s)} + 0.75\ S_{2\,(g)}$$

Partial Oxidation

The formation of elemental sulfur when metal sulfide is reacted with oxygen and steam under "O_2-starved" conditions is referred to as partial oxidation. The general stoichiometric reaction is:

$$MeS_{(s)} + 0.5\ O_{2\,(g)} \rightarrow MeO_{(s)} + 0.5\ S_{2\,(g)}$$

In reality, this stoichiometry represents the net result of a number of simultaneous reactions. In the presence of excess oxygen, total oxidation would occur with MeO (s) and SO_2 (g) as the primary products.

The bulk of research on regenerable sorbents has been on zinc-based sorbents because sorbents based on zinc oxide appear to have the fewest technical problems among all sorbents. Among the tested metal oxides ZnO has the highest equilibrium constant for sulfidation, yielding H_2S removal down to a fraction of 1 ppmv. Its principal limitation is that in the highly reducing atmosphere of synthesis gas it is partially reduced to elemental zinc. It is volatile above 600 °C, with consequent sorbent loss. Zinc Oxide is highly efficient desulfurizer due to favourable thermodynamics in the temperature range of 350-550 °C. ZnO shows low equilibrium H_2S concentration. H_2S absorption by ZnO is considered to be controlled by the following reaction:

$$ZnO_{(s)} + H_2S_{(g)} \rightarrow ZnS_{(s)} + H_2O_{(g)}$$

This is an exothermic reaction and the equilibrium H_2S concentration is determined by the temperature, the H_2S partial pressure and to a lesser extent the phase of the zinc oxide. Equilibrium H_2S concentration for ZnO with no H_2O is shown in Fig. 4. The data is generated using the HSC software. Thermodynamically, it is impossible to reduce the sulfur concentration to less than 100 ppbv at temperatures above 300 °C. At lower temperatures of (< 250 °C), absorption kinetics are slower but the ZnS equilibrium is more favorable. The data in the table indicates that if the kinetics of H_2S absorption is sufficiently rapid, concentrations well below 100 ppb should be achievable.

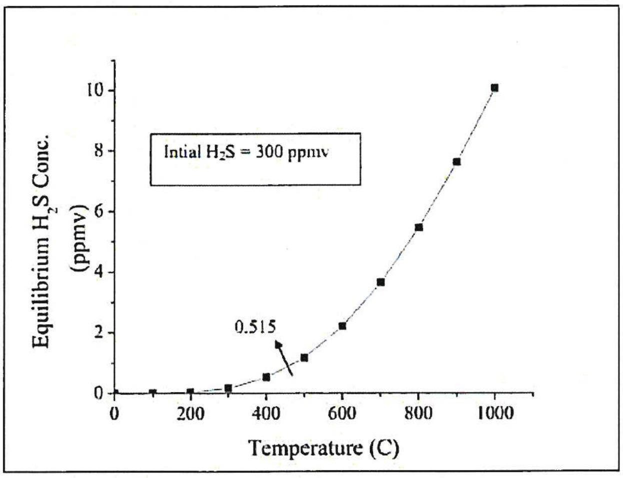


Fig. 4: Equilibrium H_2S concentration (ppmv) using HSC software

Table 1. Equilibrium data for ZnO sulphidation reaction by HSC software

T (°C)	Equilibrium constant (K)	H_2S outlet (ppmv)
0	5.32E+13	4.11E-05
200	7.60E+07	3.44E-02
400	3.39E+05	5.15E-01
600	1.82E+04	2.20E+00
800	2.92E+03	5.45E+00
1000	8.30E+02	1.01E+01

Current experiences and development status

A key application of this technology is found in the gas purification process that, after removing water-soluble halides and other contents with a water scrubber, desulfurizes the gas with a methyldiethylamine (MDEA) or other amine-based liquid absorbent for gas purification. This method, however, requires the gas to be cooled to around room temperature, thus losing much heat. Furthermore, the process becomes complex since it requires not only a heat exchanger but also a catalyst that converts hard-to-remove COS into H_2S. It is also difficult to precisely reduce sulfur compounds to a 1 ppm level. To solve problems relating to the wet gas purification process, efforts are now underway to develop dry gas purification technology that purifies hot coal gasification gas as it is. The development of hot gas cleanup (HGCU) systems for acid gas and particulates removal from syngas has been pursued in the U.S., Europe, and Japan since the 1970s. Until about the mid- 1990s, this work was primarily focused on syngas from air-blown gasification of coal. Air- blown gasification systems produce over twice the volume of syngas (due to the nitrogen dilution) that O_2-blown systems produce, and therefore incur more severe thermal, process efficiency, and capital cost penalties related to syngas cooling to comparable temperature levels. Conventional cold gas cleanup (CGCU) with air-blown systems is uneconomical. Hence, the success of air-blown gasification combined cycle power plants depends on the success of HGCU developments. However, HGCU is also applicable to syngas from O_2-blown gasification, so that O_2 gasification also would benefit from the successful development of competitive HGCU systems.

Drivers for HGCU:

The drivers for HGCU in IGCC have been:

- The higher process efficiency achievable without syngas cooling and removal of water from the syngas;
- The elimination of sour water treating. (Sour water is produced when the syngas is cooled below the dew point of water.);
- The elimination of the "black mud" (troublesome ash-char-water mixture) produced in water-quenching or wet scrubbing of particulates from the syngas;
- Potential capital and operating cost savings related to the foregoing items.

Clean coal technologies in Japan:

In Japan the development of this process as a technology for integrated gasification combined-cycle power generation (IGCC) was promoted, with a target of reducing sulfur oxides to 100 ppm or less in a temperature range of 400-500 °C, where economical carbon steel can be used for piping. Iron oxide was selected as the metal oxide to be used and Ishikawajima-Harima Heavy Industries Co., Ltd. built a fluidized-bed desulfurization pilot plant (Fig. 5) that can treat all of the coal gas, using 100-200 μm iron ore particles. It was verified in the 200-ton/day Nakoso IGCC pilot plant (1991-1995). The Central Research Institute of Electric Power Industry and Mitsubishi Heavy Industries, Ltd., with an eye to applications in the fixed-bed desulfurization systems (Fig. 6), have jointly developed an iron oxide-based honeycomb desulfurization agent. They also built, under the 200-ton/day Nakoso IGCC pilot plant project (for coal gas production of 43,600 m^3N/h), a pilot plant that can treat one-tenth of the amount of coal gas produced [18]. The performance of the honeycomb desulfurization agent is being verified. Meanwhile, Kawasaki Heavy Industries, Ltd. has developed an iron oxide-based highly wear-resistant granular desulfurization agent for use in a moving-bed combined-desulfurization/dust collection system (Fig. 7) and evaluated its performance in a pilot plant capable of treating one-fortieth of the coal gas produced by the the 200-ton/day Nakoso pilot plant. This indicates that technologies for IGCC have already reached a validation stage [19].

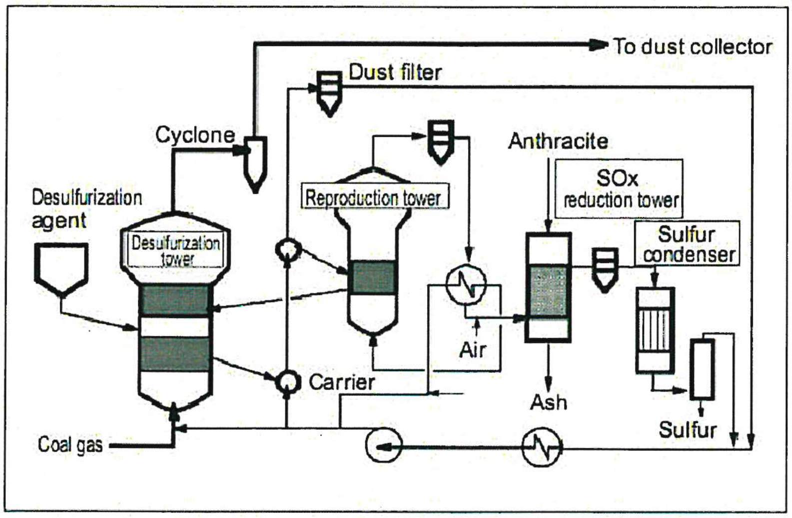


Fig. 5. Fluidized-bed desulfurization process

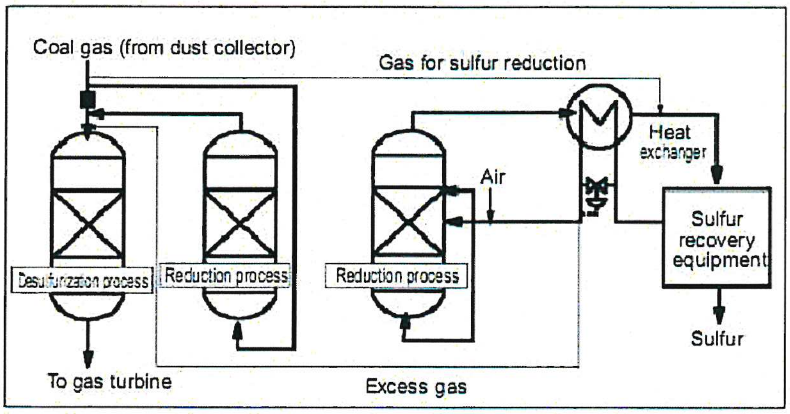


Fig. 6. Fixed-bed desulfurization process

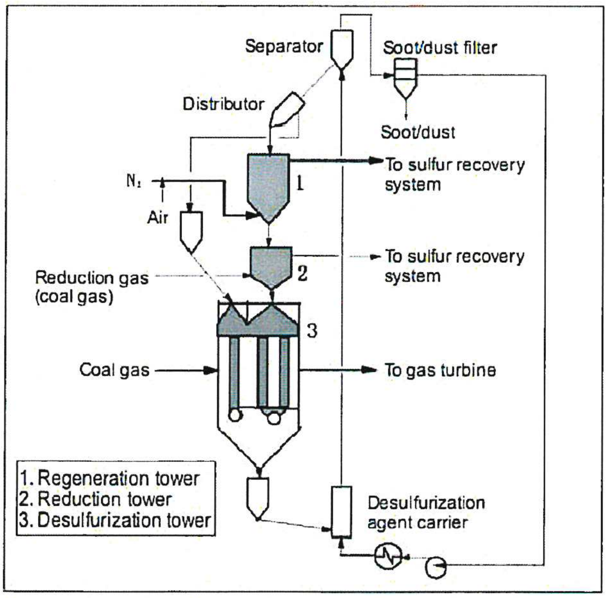


Fig. 7. Moving-bed combined dust collection-desulfurization process

At present, a desulfurization agent that can reduce sulfur compounds to a level of 1 ppm is under development for use in such applications as molten carbonate fuel cells, solid oxide fuel cells, and fuel synthesis. At the Central Research Institute of Electric Power Industry (CRIEPI), a desulfurization agent using zinc ferrite ($ZnFe_2O_4$), a double oxide of iron and zinc, has been developed and found capable of reducing sulfur compounds to 1 ppm or less. It is now at the stage of real-gas validation.

RTI International and Eastman Chemical Company:

RTI, in partnership with Eastman and DOE, has developed a novel technology package to remove various contaminants, including sulfur, ammonia, HCN, hydrogen chloride, heavy metals (Hg, As, Se, and Cd), and CO_2, from syngas produced from gasification of coal/petroleum coke at temperatures above 200 °C). Removing these contaminants without cooling the syngas (as required by conventional cleanup technologies) results in significant thermal efficiency improvements for integrated gasification combined cycle (IGCC) power plants, as shown by an independent techno-economic evaluation. This modular technology package can also meet the more challenging syngas cleanup requirements for production of chemicals and fuels from the syngas. Figure 8 shows a process low diagram depicting integration of this modular syngas cleanup package within an IGCC plant [20].

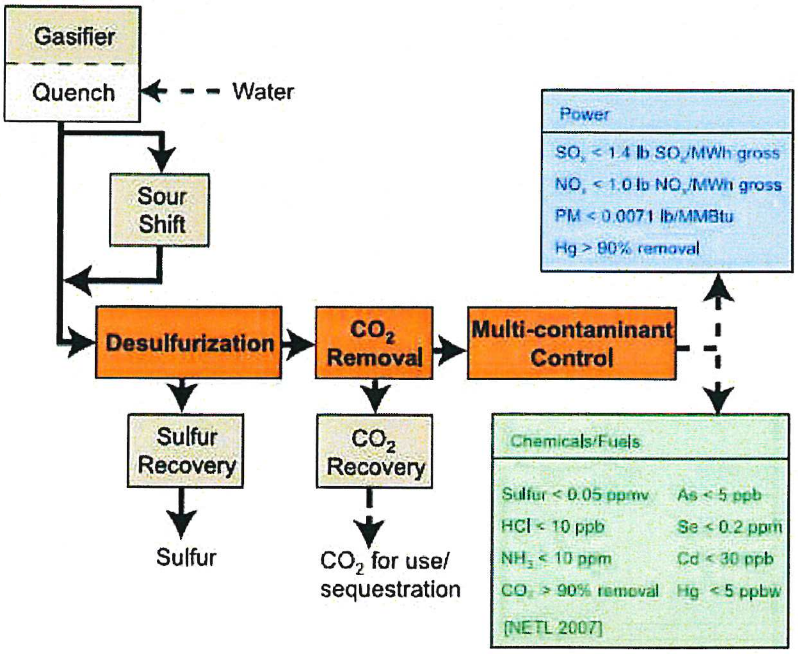


Fig. 8. Integration of RTI-Eastman Syngas Cleanup Technology in an IGCC Plant

High-Temperature Syngas Desulfurization Process (HTDP):

RTI and Eastman developed a new high-pressure dual-loop transport reactor design for HTDP. This transport reactor offers the following advantages compared to a fixed-bed process:

1. Continuous syngas desulfurization and sorbent regeneration using only two reactors;
2. Superior gas-solid contact, resulting in more efficient sulfur removal;
3. Thermally neutral operation and regenerator temperature control by heating incoming sorbent with exothermic regeneration heat:
4. Higher throughput due to high gas velocities, resulting in smaller reactor equipment for sulfur removal, and hence significantly lower capital cost.

Transport reactors have been used for several decades in the reining industry for fluid catalytic cracking. Therefore, significant design and operating experience exists for these reactors. RTI and Eastman have successfully leveraged this reactor technology for a higher-pressure operation for optimal integration within an IGCC process. The key process components are shown in Figure 9. In a parallel development track to HTDP, RTI developed a fluidizable, highly attrition-resistant, highly reactive desulfurization sorbent to meet the performance requirements of the HTDP transport reactor. This sorbent incorporates zinc oxide as the active component for the desulfurization reaction and is very effective in desulfurizing syngas between 260 °C and 540 °C. Production scale-up of the sorbent material was conducted in collaboration with a major catalyst vendor. In extended pilot-plant tests, the desulfurization sorbent exhibited excellent physical strength and activity retention.

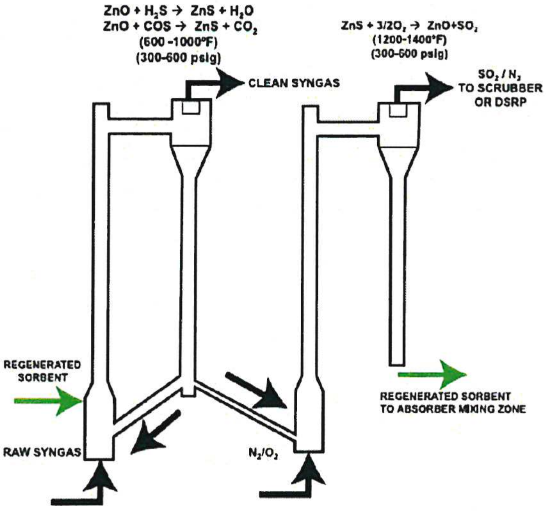


Fig. 9. Transport Reactor System Design in HTDP

Desulfurization Performance:

The HTDP pilot unit was operated for more than 3,000 hours using a syngas slipstream at Eastman's coal gasification facility in Kingsport. With an inlet syngas sulfur concentration between 7,000 and 10,000 ppmv, the effluent syngas sulfur concentration was consistently <10 ppmv (~99.9% sulfur removal efficiency) throughout testing, with <5 ppmv sulfur being consistently achieved at optimal operating conditions. The sorbent also effectively removed the COS present in syngas in addition to H_2S, as shown in Fig. 10.

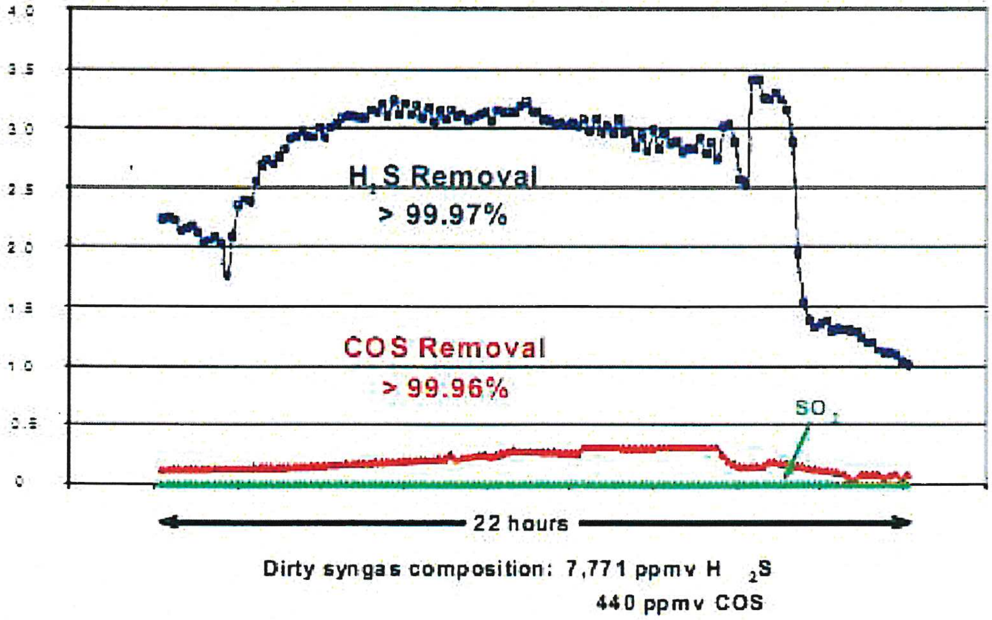
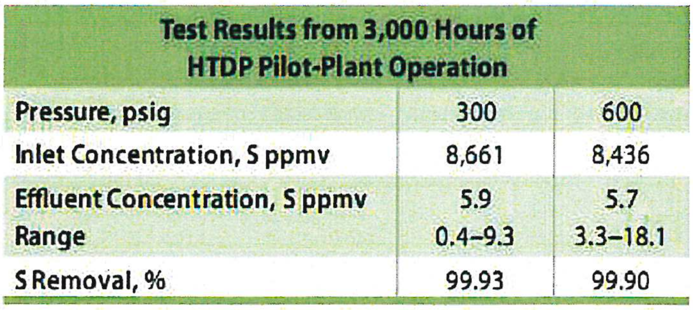


Fig. 10. Typical H_2S and COS Removal Performance of HTDP

Operational Stability:

Overall, more than 3,000 hours of successful testing of the HTDP pilot plant (Fig. 11) with coal-derived syngas was completed, with the longest period of continuous operation being over 350 hours. In addition to demonstrating long-term stable operation of the HTDP, this test also demonstrated thermally neutral operating conditions, established operating controls providing stable solids circulation and process performance, and identified and tested start-up and shutdown protocols for a commercial system.



Test Results from 3,000 Hours of HTDP Pilot-Plant Operation

Pressure, psig	300	600
Inlet Concentration, S ppmv	8,661	8,436
Effluent Concentration, S ppmv	5.9	5.7
Range	0.4–9.3	3.3–18.1
S Removal, %	99.93	99.90

Fig. 11. HTDP pilot plant

Economic Advantages:

An independent, comprehensive, techno-economic assessment of the high-temperature syngas cleanup technology package developed by RTI and Eastman for power production was performed by Nexant, Inc. In this techno-economic evaluation, Nexant compared the RTI-Eastman syngas cleanup technology package with a Selexol acid gas removal process in a state-of-the-art, 600 MWe IGCC conceptual plant incorporating the General Electric/Texaco gasifier. For both cases, cost estimates were developed for overall performance, as well as capital and operating and maintenance costs. The comparison showed that integration of the RTI-Eastman high-temperature syngas cleanup package can increase IGCC thermal efficiency by 3.6 points HHV, a relative improvement of 9.6% in power plant efficiency (Table 2). This increase in thermal efficiency is primarily due to the avoidance of process steam condensation. The estimated capital cost of the overall IGCC with high-temperature syngas cleanup case was about 15% below that of the IGCC with conventional cleanup, resulting in an approximate 10% reduction in the overall cost of electricity. These results have been confirmed in a second independent study funded by DOE as part of DOE's evaluation of emerging technologies. A similar techno-economic evaluation of the high-temperature syngas cleanup package meeting contaminant specifications for chemical/fuel production applications is currently being conducted with and without CO_2 capture.

Table 2. Techno-economic evaluation, comparing the RTI-Eastman syngas cleanup technology package with a Selexol acid gas removal process in a state-of-the-art, 600 MWe IGCC conceptual plant incorporating the General Electric/Texaco gasifier

	IGCC Base Case	IGCC with Warm Syngas	Improvement (%)
Imports/Feeds			
Coal Feed, STPD (AR)	5,467	5,467	
95% Oxygen, STPD	4,665	4,895	-4.9
99% N_2, STPD	7,024	3,959	43.6
Make Up Water, GPM	5,646	4,288	24.1
Exports or Products			
Electric Power, MW	585	641	9.6
Waste Water, GPM	2,798	1,085	61.2
Thermal Efficiency			
HHV%	37.6	41.2	9.6
LHV%	39.3	43.1	9.7

Proposed Project:

RTI International (RTI) in October 2011 [20] has presented its proposed project to demonstrate the pre-commercial scale-up of RTI's high-temperature syngas cleanup and carbon capture and sequestration technologies. RTI's proposed project would be located at Tampa Electric Company's existing Polk Power Station in Polk County, Florida. The proposed project would treat a slipstream, equivalent to up to 66 megawatts of electricity generation, of coal-derived syngas from the existing Polk Unit 1 integrated gasification combined-cycle power plant to remove 99.9% of the sulfur, reduce trace contaminant (arsenic, selenium, and mercury) concentrations, and convert the removed sulfur compounds to commercial-grade elemental sulfur. Also, up to 300,000 tons per year, or 90 percent, of the carbon dioxide (CO_2) in the cleaned syngas would be captured and sequestered in a deep geologic formation and not released to the atmosphere.

High-Temperature Desulfurization Process:

A slipstream of syngas from the IGCC plant with a flow rate of up to 2 million standard cubic feet per hour (MMSCFH), which would be equivalent to up to 66 MW of electric power, would be treated in the HTDP system. The untreated syngas would contain a hydrogen sulfide (H_2S) concentration of approximately 7200 ppmv. The HTDP system consists of two coupled transport reactors, the first serving as the sulfur absorber and the second as the sorbent regenerator. The sulfur absorber utilizes chemical reactions with RTI's proprietary sorbent to remove H_2S and carbonyl sulfide (COS) from the syngas to produce a syngas with a total sulfur concentration of less than 10 ppmv. In the sorbent regenerator reactor, the sorbent is regenerated by oxidizing the sulfur compounds to produce a flue gas stream containing SO_2. Most of this stream would be directed to Tampa Electric's existing sulfuric acid plant, where the SO_2 would be converted to sulfuric acid. As part of the proposed project, a small portion of this SO_2 stream would be routed to the DSRP system. The HTDP system would involve several intermittent sources of air emissions. During startup of the system, a propane-fired heater, which is vented to the atmosphere, would be used to heat the absorber and regenerator systems. During startups, the regenerator is further preheated using distillate fuel oil. The syngas initially introduced into the absorber and regenerator gases would be sent to Tampa Electric's existing flare to minimize impacts on downstream processes (i.e., combustion turbine and steam turbine), while the gas does not meet specifications during start-up. Also, intermittent particulate matter (PM) emissions would occur from the vented sorbent storage hopper and regenerator fines bin.

Hot gas desulfurization demonstrations in the U.S.A.:

The only two large-scale "hot gas" desulfurization systems installed in the U.S. both in DOE CCT IGCC demonstration projects have never been demonstrated. Consequently, their ultimate commercial feasibility may never be known. Both systems were similarly based on the reaction of H_2S with zinc oxide-nickel oxide solid sorbents in an adsorption column followed by regeneration of the sorbent by contact with air in a separate column. The regenerator off-gas contains SO_2, which must be converted to elemental sulfur or sulfuric acid in a final recovery operation. There are no large-scale hot or warm desulfurization demonstrations elsewhere. The systems are briefly described further below. The 260 MW coal-fired IGCC at Tampa Electric Company's (TECO's) Polk County Station in Florida (Texaco gasification process with a radiant syngas cooler, convective coolers, and water scrubbing) is equipped with both a 100% capacity CGCU system and a 10% capacity HGCU system to be fed by a syngas slipstream. The plant is operating well with the CGCU system. The HGCU was based on a down-flow moving-bed H_2S adsorption process developed by GE. The design placed the absorber column on top of the down-flow regenerator column in one tall column. The regenerated sorbent is transported back to the top of the column. The SO_2 was to be converted to sulfuric acid for sale. Some observers have noted that the physical size of the 10%

capacity HGCU appears to be much larger than that of the 100% capacity CGCU section of the plant. The HGCU demonstration was cancelled for the following reasons:

1. The fouling factors in the waste heat boiler (radiant syngas cooler) were not as severe as predicted. Consequently, heat recovery was more efficient and the syngas was cooled to about 370 °C a much lower temperature than expected. A temperature of at least 480 °C is needed for the HGCU.
2. Cold flow attrition tests on the sorbent showed that sorbent attrition would be very high leading to extremely high annual sorbent costs.
3. There were also concerns about the potential for chloride stress corrosion cracking with the materials used in the HGCU [21].

The Piñon Pine IGCC system in Nevada is designed with a KBR air-blown, fluidized-bed gasifier (operating at 980 °C) with limestone injection for partial in-situ H_2S capture (as CaS) followed by final H_2S scrubbing from the syngas in an entrained-flow absorber. Unfortunately, numerous problems with solids transport (fly ash) in the gasifier system have prevented successful start up [22], and it appears that this DOE CCT Program demonstration project has been terminated. The Piñon Pine flow scheme employs entrained-flow H_2S adsorption and regeneration columns called transport reactors by KBR. The coal ash-char-CaO-CaS solids from the gasifier, the SO_2 from the regenerator, and additional limestone, are fed to a "sulfator" a bubbling fluidized bed combustor in which most of the sulfur is converted to $CaSO_4$. Thus SO_2 emissions from this plant would come from both the GT exhaust gas and the sulfator. As in the TECO case, pre-startup testing indicated excessive sorbent attrition. As of the last start-up attempts (2000), a sulfur sorbent with satisfactory mechanical durability had not been identified [23]. It is instructive for future scale-up considerations to note that this 880 t/d gasifier design was a high-risk 40-fold scale-up from the successful 20-24 t/d pilot plant program in which the KBR gasifier was developed. Also, although the desulfurization transport reactor is patterned after proven catalytic reactors used in petroleum refining, the desulfurization system (including a qualified sorbent) itself was not previously demonstrated at an intermediate scale. At the Berrenrath High-Temperature Winkler (HTW) gasification demonstration plant, Rheinbraun reportedly tested a technique called direct desulfurization or direct sulfur recovery. Apparently the addition (or presence) of a metal oxide catalyst into the gasifier or the syngas stream is required in this process, and an oxygen-containing gas is added to the syngas after the syngas cooler but before the candle filters at a temperature of about 200-270 °C. Rheinbraun claims that its tests at Berrenrath show that the H_2S is completely converted into elemental sulphur, while the COS is partly converted. The sulfur (solid particulates) and the dust are separated from the syngas by the filter. Ammonia is not removed in this process. This process has been proposed for testing with a slipstream at the planned 400 MW HTW IGCC plant at Vresova in the Czech Republic. DOE and DOE-sponsored researchers have also been investigating variations on this process.

Continuing DOE and EPRI Warm Gas Cleanup Programs:

Three long-running DOE-supported R&D programs on warm gas cleanup continue at Siemens Westinghouse Power Corporation (SWPC), Research Triangle Institute (RTI), and the Power Systems Development Facility (PSDF) operated by Southern Company Services at Wilsonville, Alabama. EPRI is also providing support for the PSDF program, along with the Southern Company. SWPC's activities include: the assessment of barrier filter materials and filter performance, the development of a candle filter failure safeguard device (SGD), and R&D on a conceptual 4-stage process that the investigators are calling the "Ultra-Clean Process." While this process is targeting removal of H_2S, HCl, and particulates to sub-ppm levels, it does not remove NH_3, HCN, or mercury [24]. A 10 t/d fluidized bed gasification pilot plant is being constructed at the Gas Technology Institute (GTI) for testing the "Ultra-Clean Process." RTI is investigating a conceptual multi-step process that includes $H_2S/CO_2/H_2O$ removal by a solubility-selective polymer membrane, recovery of elemental sulfur by RTI's Direct Sulfur Recovery Process (DSRP), and removal of ammonia by zeolite molecular sieves. While the work is targeting very low emissions levels, rapidly decreasing membrane selectivity as temperature increases above 25 °C is a challenge. The other participants in this program are DuPont, Air Liquide, North Carolina State University, Prototech Company, SRI International, and Nexant. The PSDF facilities include a 1.6 t/hr KBR transport reactor, SWPC particulates control devices, (PCDs – with candle filters), and a low-NO_x topping combustor with an Allison 501-KM gas turbine generator set (4 MW nominal). The transport reactor can be operated in the combustion mode or gasification mode. One of the PSDF's earlier anticipated uses was to have provided R&D support to the now defunct Piñon Pine IGCC demonstration. From DOE's perspective, the primary focus of the PSDF now is to demonstrate and evaluate the transport reactor and high- temperature, high-pressure PCDs for advanced power generation systems, such as GT combined cycles and fuel cells. The transport reactor is also part of the research portfolio for DOE's Vision 21 program, which includes evaluating the KBR reactor as a potential commercial gasifier and possibly using the facility for HGCU R&D [25]. Overall, the ambitious DOE/EPRI/Southern Company program for the PSDF included tests of both air- and O_2-blown KBR reactor gasification, hot gas filtration, ash removal, hot gas desulfurization, sulfur recovery, and trace element and mercury removal from syngas [26].

Outlook and areas to be improved

The development of hot gas cleanup systems for deep cleaning of sulfur components from syngas appear to be long-term prospects. Large-scale demonstrations have not been achievable or practical before about 2010. Justification for such demonstrations could become difficult if commercial IGCC projects with CGCU continue to proliferate and operate well over the next several years.

Overview:

To overcome the inefficient low-temperature cleaning, several options for high-temperature gas cleaning from sulfur impurities are proposed. For these applications, efforts are underway to develop a H_2S sorbents capable of reducing to 1 ppm or less. At present, much of the research in the past two decades has focused on stabilization of these materials through formation of mixed oxides. The "optimum" sorbent depends on process conditions and target sulfur levels. Rare earth-based sorbents show significant promise for high temperature applications (700-850 °C). Manganese- and zinc titanate-based sorbents also have potential for applications in the 700 °C range if care is taken to limit sulfate formation. Both manganese- and ceria- based materials may be regenerated with the direct production of elemental sulfur. Copper-based and zinc ferrite materials are well suited for approximately 500 °C. Unmodified zinc oxide-based materials are generally more applicable to the low temperature ranges. Although has been done enough from a point of view of the research, it will has to do still much for a future industrial application of this "new" technology. For mid-temperature desulfurization, further research is necessary to determine the performance of sorbents in a high steam environment containing light hydrocarbons and tar. An understanding of the extent of removal of other sulfur species such as COS is also essential. There is increasingly more research on binary oxides and "promoted" binary oxides to determine whether these modified materials provide better attrition resistance, higher sulfidation equilibrium constants, and the ability to remove multiple gas contaminants. Key remaining questions include whether multiple contaminants in syngas can be removed simultaneously and whether one contaminant might interfere with the removal of another. With information on syngas contaminant concentrations and speciation, the appropriate sorbents and "multifunctional" materials can be better designed and tested in the laboratory. Pilot scale testing of such sorbents will provide results and experience for eventual commercialization. As more scientific data on mid- to high-temperature sulfur sorbent becomes available, techno-economic analysis and systems modelling to determine the potential improvements in thermal efficiency, environmental benefits, and process economics through use of such sorbent systems will be critical. In the research, metal oxides have been used as sorbents in sulfur removal for about 70 years, and they share some common issues, including the issues related to their intrinsic properties and the issues related to their properties of their existence. These drawbacks will be meet again when get on large- scale plants. The first issue is oxide reduction in fuel gases containing H_2 and/or CO. It is very possible for the metal ion (M^{2x+}) in MO_x to be reduced to any low oxide states or metallic, depending on the reducibility of fuel gases. Reduced metal oxides or metallic normally have lower sulfur capacity than these in high oxidative states. For example, pure Fe_2O_3 has a stoichiometric capacity of 0.6 g S/ g Sorbent, while FeO, 0.444 g S/ g Sorbent. Another worse effect is that the reduction makes the sorbent structure collapse in some cases. Moreover, sulfidation kinetics decreased slightly after the reduction of metal oxides. Sometime, the reduction of metal oxides to metallics may cause detrimental effects on sulfidation, because metallics have much lower equilibrium constants than metal oxides, and they cannot remove H_2S to very low levels, e.g. copper oxides, iron oxide. The third drawback for metallics is the formation and growth of metal clusters. Metallics tend to grow into large clusters thus decrease the surface area or block the pores, making active sorbent inaccessible. For example, Co and Cu are ready to reduce by coal gas [27]. Moreover, for some volatile metals, i.e., zinc and lead, the formation of metallic is a disaster for sorbents. It causes metal vaporization and subsequent metal loss.

Equilibrium Constant at High Temperatures

Another intrinsic phenomenon of metal oxides is their degrading equilibria at high temperatures. For most metal oxides, the equilibrium constants of sulfidation decrease with temperature increases. The decrease in equilibrium constant means the increase in equilibrium H_2S concentration. For example, although MnO sorbent can remove H_2S to 1 ppmv at 300 °C, it becomes impossible at 600 °C. Therefore, metal oxides with low equilibrium constants are not favourable for deep desulfurization at high temperatures. Sorbent based on rare earth metals, such as Lanthanum oxide (La_2O_3) and cerium oxide (CeO_2) demonstrated potential to remove sulfur to extremely low concentration even at high temperatures (>800 °C), though their sulfur capacities need further improvements for practical applications.

Surface Area Loss

It is critical to maintain high surface area and pore structure of the sorbents especially for multi-cycle applications. At low temperatures, e.g. room temperature, only the active chemicals in the first monolayer can be accessed by H_2S. The more active chemicals in this monolayer, the larger capacity the sorbent has. It means that a sorbent with high surface area will certainly have a high capacity and breakthrough capacity (or dynamic capacity) for low temperature applications. The sorbents of active chemical supported on inert particles with high surface area will performance at least as well as the sorbent made of pure active chemical in the respect of sulfur capacity at low temperatures. The high surface area is not as important for desulfurization at a high temperature as it is at low temperatures, because more active chemical can be accessed due to the faster mass transfer at high temperatures. However, the high specific surface area is still a helpful to enhance the breakthrough capacities. The more specific surface area the sorbents have, the faster the intrinsic reaction rate can be reached. However, it is almost impossible to maintain the high specific surface area of regenerable sorbents during multi-cycles. Actually, surface area loss is a very common phenomenon during spent sorbent regeneration due to the growth of grains [14, 28, 29]. Companying with the surface area loss, the loss in pore volume is another widely observed phenomenon during high temperature desulfurization or regeneration. The reduction in porosity significantly increases the pore diffusion resistance and severely decelerates the reaction rate. Therefore, to maintain the high surface area and high porosity become critical for successful sorbent and/or catalyst designs. In order to maintain the surface area and porosity of sorbents, the active sorbent substances are mixed with other oxides. The first mixed oxide scheme is to support active chemicals on a secondary oxide support. These secondary compounds are mainly inert to sulfur, such as Al_2O_3, monolith, SiO_2, TiO_2, zeolite, and the functions of supports are: (1) to provide a good structure stability for the sorbent; (2) to hold the sorbent grains in the micropores and prevent increase in grain size and agglomeration, therefore maintain the high surface area, high porosity and high sorbent capacity; (3) to stabilize the active metal oxide sorbent from reduction and vaporization. The supported sorbent design may also facilitate the incorporation of sorbent into systems, such as the monolith supported metal oxide sorbents designed by Engelhard. Due to the advantages of using supports, the sorbents provides stable performance with extended service life.

Attrition

For industrial applications, metal oxide sorbents are typically prepared in form of pellets, widely used in fixed- and moving beds. Sorbent pellets mainly consist of primary active metal oxides, secondary metal oxides (promoter), stabilizers and binders. For example, in zinc titanate sorbent, zinc oxide is the primary activate metal oxide; Mo, Ni based oxides are secondary oxides used to improve the performance in sulfidation and/or regeneration; TiO_2 is the main stabilizer used to keep Zn at oxidative state; beninate is a inorganic binder used to enhance the strength of pellets. The issues discussed here are mostly related to pellets. One consideration for industrial application is attrition in fluidized bed. Gupta et al. [30] at Morgantown found that the sorbents for fluidized beds with acceptable sulfur capacity prepared by crushing the zinc ferrite pellets and screening underwent excessive attrition during multiple-cycle of adsorption and regeneration. They applied several different techniques, such as spray drying, impregnation, crushing and screening of pellets, granulation, to build sorbents with robust attrition-resistant structure for fluidized bed reactors. The results indicated that significant sorbent weakening due to chemical attrition occurred at 625 °C, and sorbents prepared using granulation technique showed good attrition resistance and maintained acceptable sulfur capacities. Attrition is also related to sorbents pellets in packed beds. After several sulfidation- regeneration cycles, sorbent pellets in fixed bed reactor are cracked and even broken into small pieces. Several factors account for this common phenomenon. The first one is thermal attrition. Because of the non-uniform temperature profile in pellets, the different thermal extension rate will gradually introduce cracks. Another reason is chemical attrition. In the sulfidation, sulfur atoms diffuse into the lattice and substitute oxygen atoms, which are smaller than sulfur atoms, therefore, the lattice structure expands; in regeneration, sulfur atoms are moved out from the lattice and substituted by oxygen atoms, and the lattice structure shrinks. The cracks develop when sulfur atoms move into and out from the lattice. Because of these reasons, active sorbents are commonly diluted by stabilizers and strengthened by binders, which are usually Al_2O_3 and SiO_2, to reduce chemical attrition and enhance the pellet integrity.

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