

5B5. Gas Cleaning Technology

Technology overview

1. Background

For the development of coal gasification gas-based power generation and fuel synthesis technologies, it is necessary to remove sulfur compounds (H₂S, COS), halides (HCl, HF), and other gas contents. As shown in Figure 1, a key application of this technology is found in the wet 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 H₂S. 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.

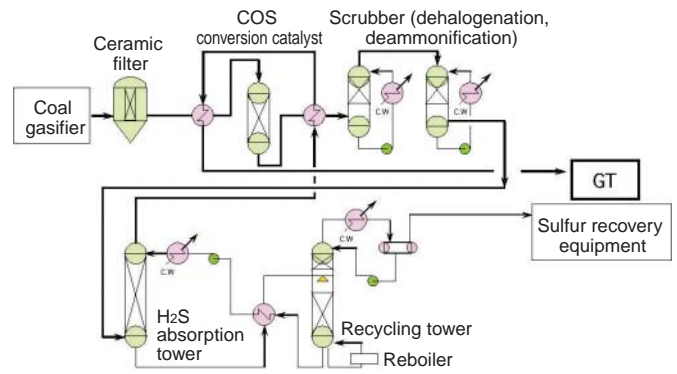


Fig. 1 Wet gas purification process

2. Technology

(1) Dry desulfurization method

Research and development: Japan Coal Energy Center; IGCC Research Association; Central Research Institute of Electric Power Industry; Kawasaki Heavy Industries, Ltd.; Ishikawajima-Harima Heavy Industries Co., Ltd.; Mitsubishi Heavy Industries, Ltd.

Project type: Entrained bed coal gasification power generation plant, etc.

Overview

As shown in Figure 2, in the dry desulfurization process, metal oxides are reduced by coal gasification gas, and the reduced metal oxides remove sulfur compounds from the gas, and are then converted to sulfides. This method can be used more than once by letting the sulfides react with oxygen to release the sulfur contents as SO₂ to return them to metal oxides.

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 100ppm 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. 3) 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. 4), 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 43,600m³N/h), a pilot plant that can treat one-tenth of the amount of coal gas produced. 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. 5) 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.

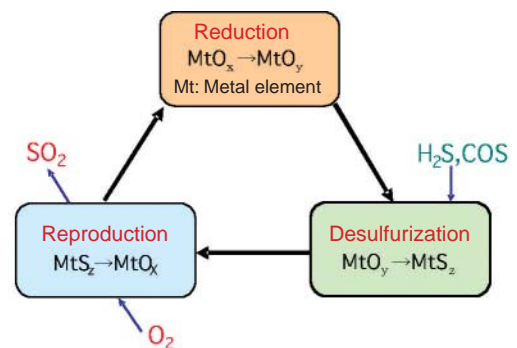


Fig. 2 Desulfurization reaction cycle

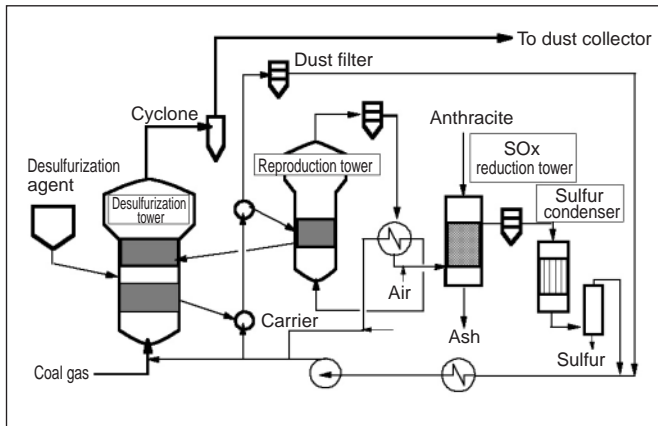


Fig. 3 Fluidized-bed desulfurization process

At present, a desulfurization agent that can reduce sulfur compounds to a level of 1ppm 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 1ppm or less. It is now at the stage of real-gas validation. In addition, efforts to introduce the desulfurization agent into air-blown entrained-bed gasification systems have been made. Another important subject is the application of the agent to oxygen-blown gasification gas with a high carbon-monoxide concentration, which degrades the desulfurization agent by allowing carbon to be separated out of it.

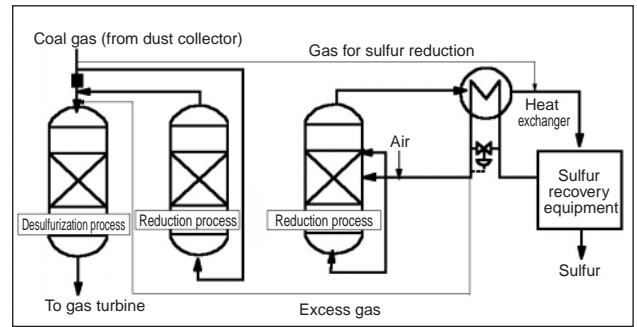


Fig. 4 Fixed-bed desulfurization process

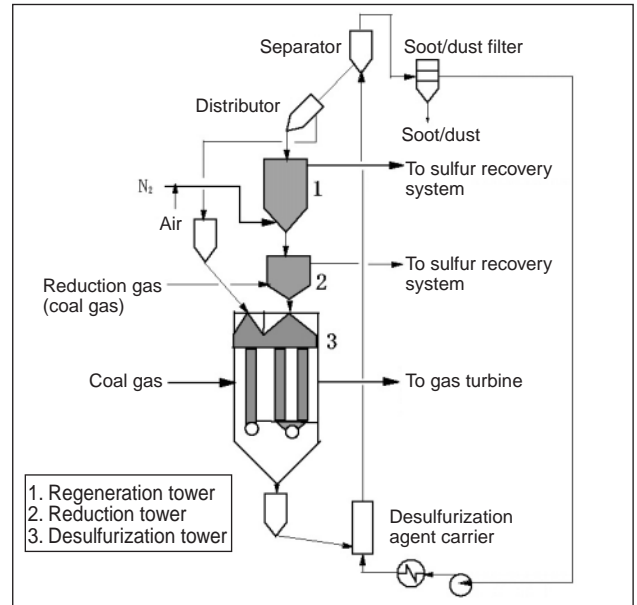


Fig. 5 Moving-bed combined dust collection-desulfurization process

(2) Dry dehalogenation method

Research and development: Central Research Institute of Electric Power Industry

Project type: Voluntary

Overview

To use coal gasification gas in molten carbonate/solid oxide fuel cells and for fuel synthesis, it is necessary to remove not only soot, dust and sulfur compounds but also halogen compounds. For these applications, efforts are underway to develop a halide absorption agent capable of reducing halogen to 1ppm or less. At present, a method to remove HCl/HF from gas as NaCl/NaF

using a sodic compound is under development. CRIEPI developed and tested a sodium aluminate ($NaAlO_2$)-based absorbent, confirming a possible reduction to 1ppm or less, but such efforts still remain on a laboratory scale as well as at a development stage. This method faces an important problem of how the absorbent should be reproduced or recycled.

References

- 1) Nakayama et al., "Development State of 3 Dry Gas Cleanup Methods in Dry Gas Cleanup Technology Development for Integrated Gasification Combined-Cycle Power Generation," the Japan Institute of Energy Journal, Vol. 75, No. 5, 1996.
- 2) Shirai et al., "Coal Gasification Gas-Based Fixed-Bed Dry Desulfurization Technology Development," the Society of Powder Technology, Japan's Journal, Vol. 40, No. 8, 2003.
- 3) M. Nunokawa et al., "Developments of Hot Coal Gas Desulfurization and Dehalide Technologies for IG-MCFC Power Generation System," CEPSI proceedings, Fukuoka, 2002.