국내고유 철광석계 탈황제 개발

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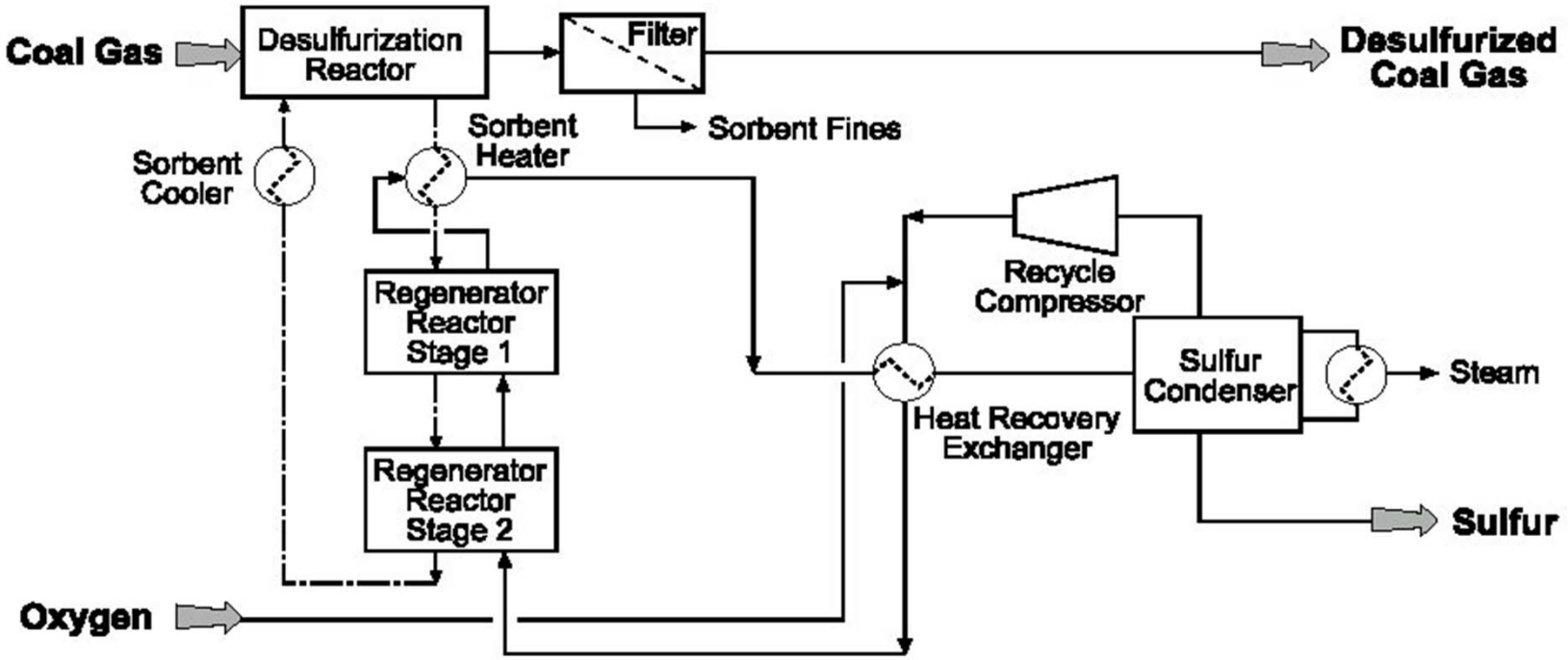
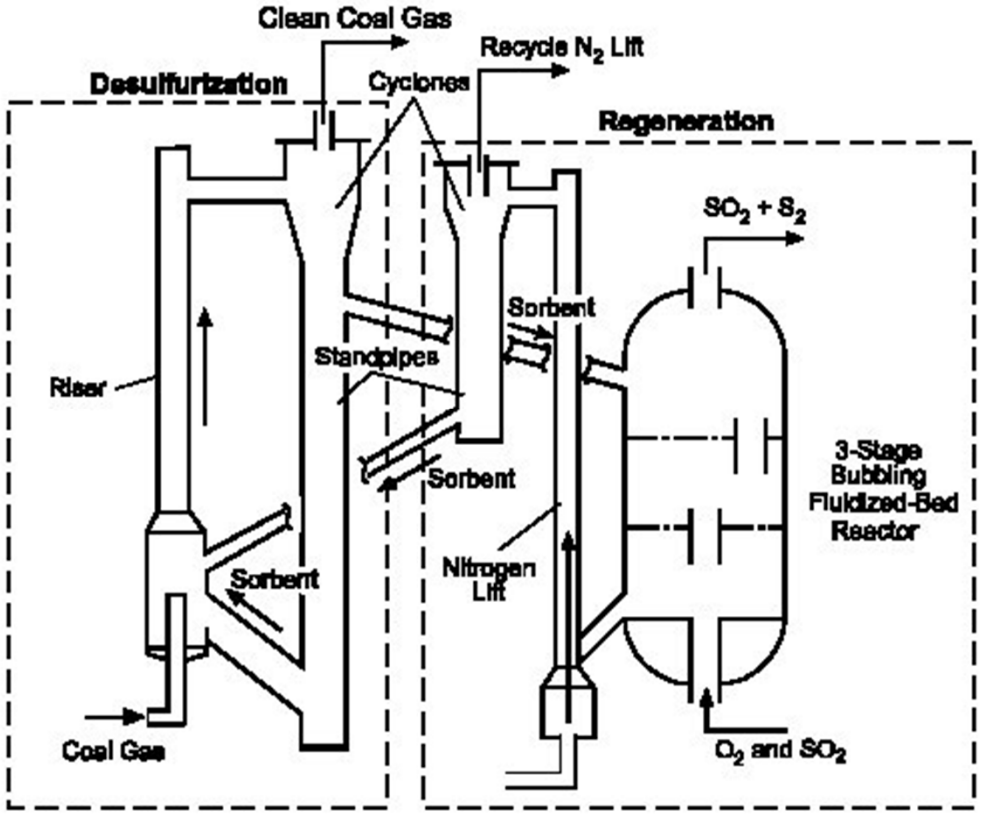
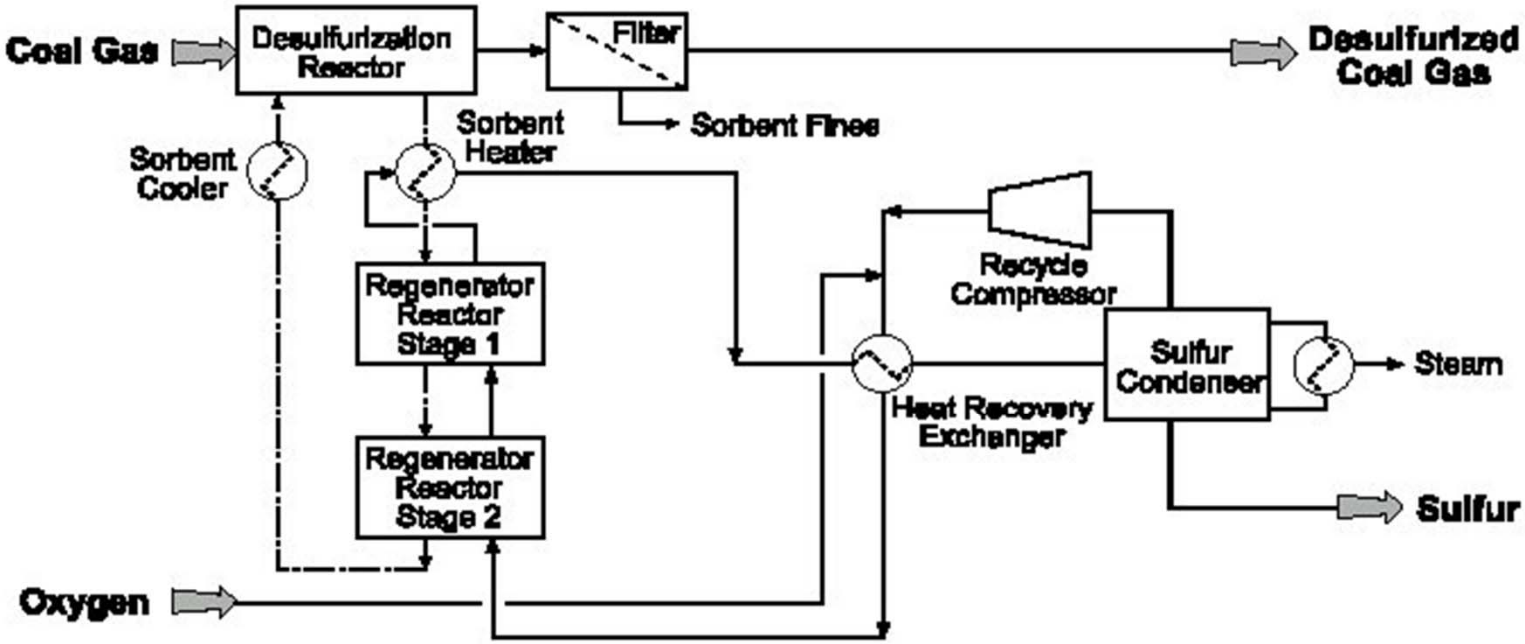
Advanced hot-gas process(AHGP)

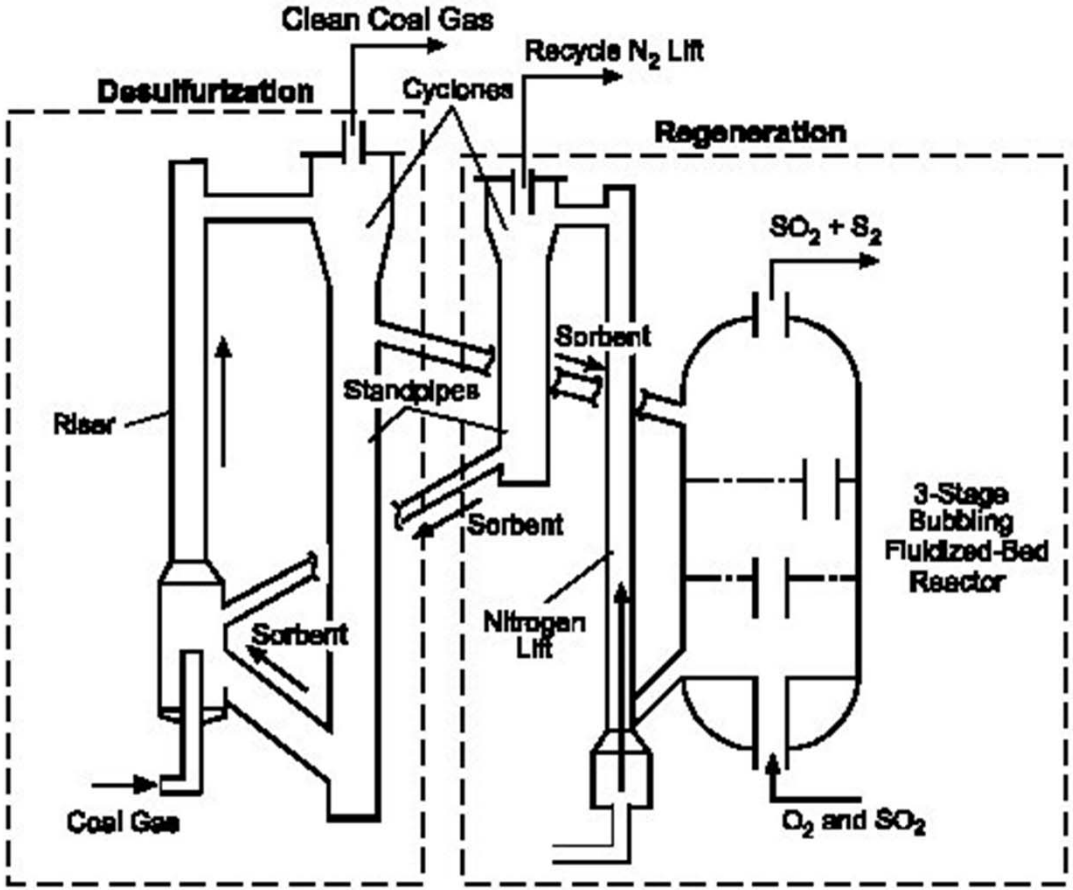


Schematic of AHGP desulfurization and regeneration reactors





Advanced hot-gas process (AHGP).



Schematic of AHGP desulfurization and regeneration reactors.

J.D. White, F.R. Groves Jr., D.P. Harrison, *Elemental sulfur production during the regeneration of iron oxide high-temp. desulfurization sorbent*", Catalysis Today **40** 47-57 (1998).

Sulfidation

$$Fe_2O_3 + 2H_2S + H_2 \rightarrow 2FeS + 3H_2O$$

Regeneration (steam-oxygen mixture)

$$2FeS + 7/2\ O_2 \rightarrow Fe_2O_3 + 2SO_2 \text{ (very fast)}$$

$$3FeS + 4H_2O \rightarrow Fe_3O_4 + 3H_2O + H_2$$

$$SO_2 + 2H_2S \rightarrow 2H_2O + 3/2\ S_2$$

$$2Fe_3O_4 + 1/2\ O_2 \rightarrow 3Fe_2O_3$$

Sulfidation (Desulfurization Reactor)

$$Fe_2O_3 + 2H_2S + H_2 \rightarrow 2FeS + 3H_2O$$

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

SO_2 Regeneration (Regenerator-Stage1)

$$4FeS + 3SO_2 \rightarrow 2Fe_2O_3 + 7/2\ S_2$$

O_2 Regeneration (Regenerator-Stage2)

$$2FeS + 7/2\ O_2 \rightarrow Fe_2O_3 + 2SO_2$$

$$ZnS + 3/2\ O_2 \rightarrow ZnO + SO_2$$

Direct Sulfur Recovery Process(DSRP)

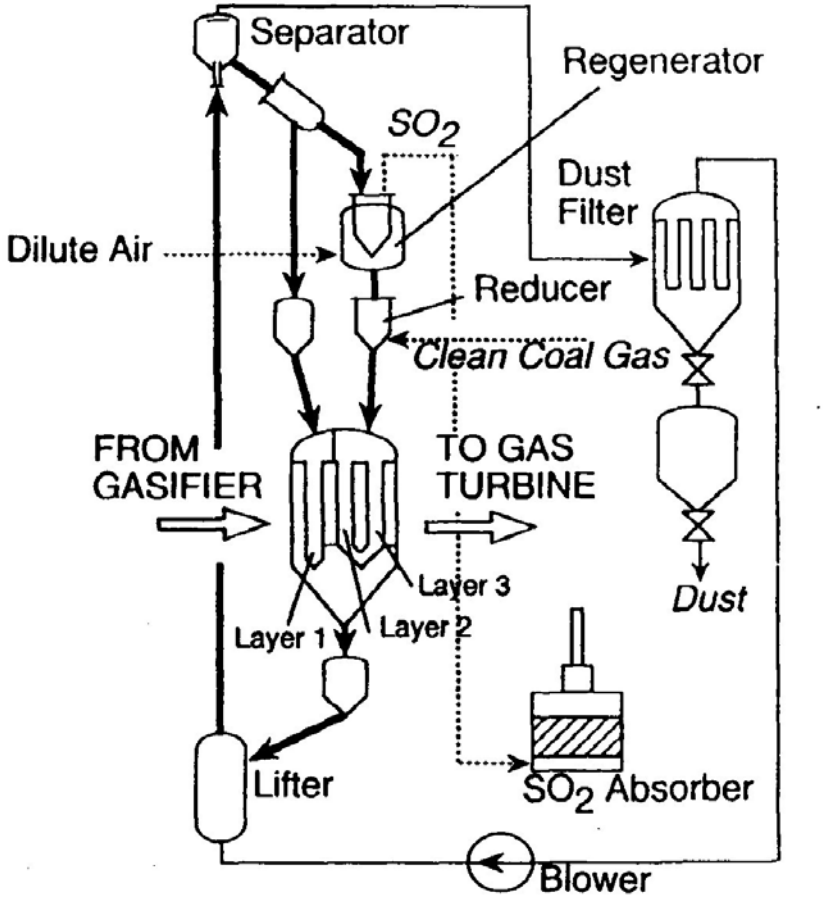
(Dorchak et al., 1991; Portzer & Gangwal,1995)

$$SO_2 + 2H_2\,(\text{or } 2CO) \rightarrow 2H_2O\,(\text{or } 2CO_2) + 1/n\ S_n$$

Using coal gas slipstream as reducing gas

Process Schematic of the 4t/d Moving Bed Hot Gas Cleanup Test Plant

Kawasaki Heavy Industries(KHI), LTD



Major results obtained from bench-scale fixed-bed experiments for HTW-based IGCC power plant (Rheinbraun AG, Germany)

Sorbent	Absorption Temperature [℃]	Regeneration Temperature [℃]	Sorbent Utilization [%]	H_2S Outlet Content [ppmv]	Major Finding
Iron(pellets)	600	600	~15	~100	reactions only on outer surface no degradation
Iron Oxide	360-400	360-400	25-45	<50	low sulphur capacity sulphate formation no degradation
Copper Oxide	550	650	~70	<20	dust formation sulphate formation no degradation
Zinc Ferrite	450-550	600	20-65	<20	severe degradation sulphate formation sulphur formation
Zinc Titanate	450-600	600	40-60	<10	severe degradation sulphate formation sulphur formation
Tin Dioxide	450	500	<85	<100	coarse H_2S removal no degradation high chemical stability
Zinc Oxide	450	500	not determined	<1	polishing step no degradation high chemical stability

The Record of Desulfurization and Dust Removal Performance of the 4t/d Moving Bed Hot Gas Cleanup Test Plant

coal	sulfur			dust particulate			operation hour
	inlet (ppmV)	outlet (ppmV)	removal efficiency(%)	inlet (mg/m^3_N)	outlet (mg/m^3_N)	removal efficiency(%)	
Taiheiyo	150-300	18-87	53.6-95.8	100-450	< 4	96.0-99.8	411
Moura	500-750	12-90	86.3-98.0	150-500	< 2	98.7-99.8	1004
Moura (sulfur added)	900-1350	17-77	92.9-98.7	250-500	< 2	98.7-99.8	174
Warkworth	520-700	19-52	90.3-97.3	200-550	< 1	>99.5	114

철광석계 고온건식 탈황제 개발현황

기관	탈황제	반응온도(℃)	탈황압력 (atm)	가스유량 (Nm^3/h)	재생온도 (℃)
Appleby-Frodingham	**Fe_2O_3**	**350～420**	**1**	**110,000**	**593～816**
Babcock-Wilcox	**FeO**	**427～649**		**170**	**538～649**
Battelle Columbus	**Fe_2O_3**	**538～816**	**1**	**0.06**	**593**
IMMR	**Fe_2O_3 (가스화로 회)**	**371～816**	**4～9**	**1**	**427～649**
IHI	**Fe_2O_3 (철광석)**	**460～550**	**1～9**	**10～50**	**550～800**
METC	**Fe_2O_3**	**538～816**	**1～20**	**212**	**538～816**

Reduction

$$3Fe_2O_3 + H_2(\text{or } CO) \rightarrow 2Fe_3O_4 + H_2O(\text{or } CO_2)$$

Sulfidation

$$Fe_3O_4 + 3H_2S + H_2(\text{or } CO) \rightarrow 3FeS + 4H_2O(\text{or } 3H_2O + CO_2)$$

Regeneration

$$2FeS + 3.5O_2 \rightarrow Fe_2O_3 + 2SO_2$$

COS conversion

$$COS + H_2 \rightarrow H_2S + CO$$

Sulfate formation (< 400℃)

$$2FeS + 5O_2 + SO_2 \rightarrow Fe_2(SO_4)_3$$

Cost Comparision : Waste Metal Oxide Sorbent

Sorbent	SO_2*	H_2S*
Iron oxide	137.79	388.70
Zinc oxide	13.84	65.14
Tin oxide	7.21	2.09

(*) in grams of S removed / dollar value of pure metal

철광석계 탈황제 특징

- 중온영역(350~550℃)에 가장 적합

  탈황능력 및 반응성 입증

- 저온재생 및 황산염 생성 제어 가능
- 직접황회수 가능

  Jeffrey W.Portzer et al., 1997 (RTI)
  D.P.Harrison et al., 1999 (LSU)

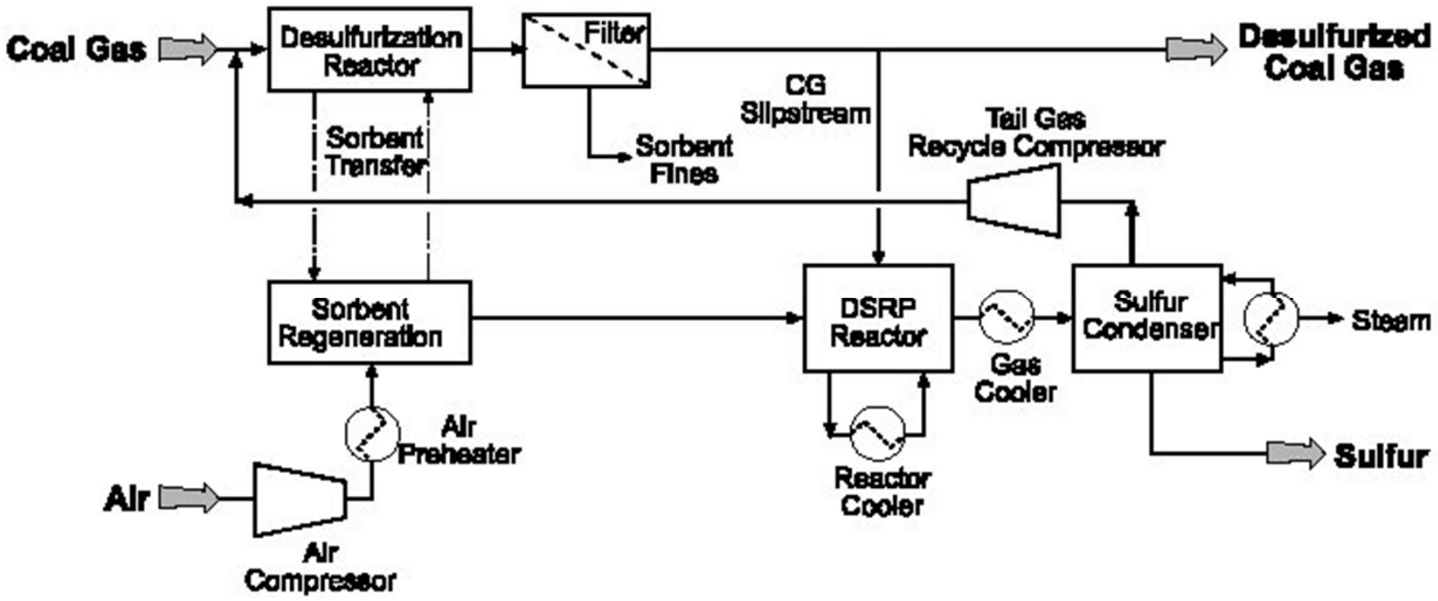
- 가장 저렴한 원료이며 구입이 용이

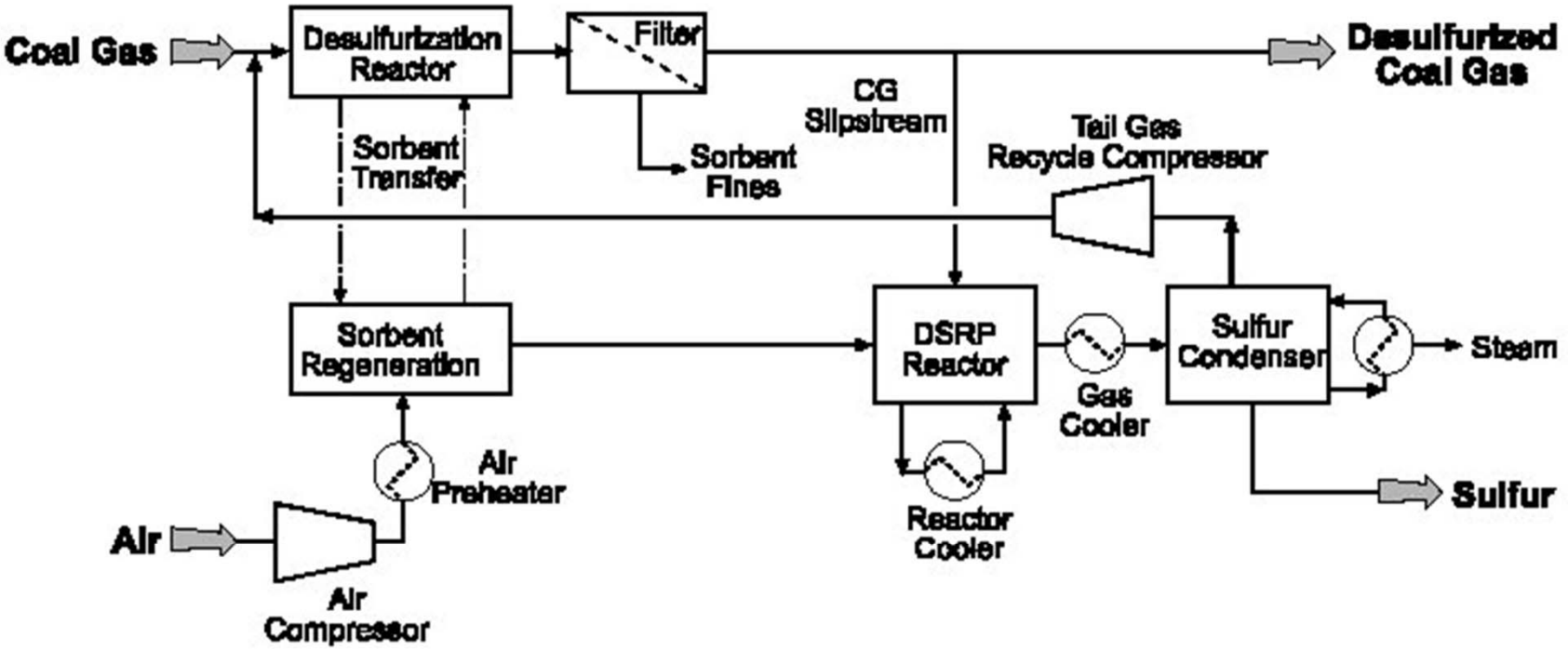
  철광석:$1.14/lb, Zinc titanate:>$3.8/lb
  Z-sorb III:>$ 7.3/lb

- 특허제약 거의 없음

  $ZnFe_2O_4$에 집중. 기타는 초보적 단계의 재질특허

Hot-gas Desulfurization with DSRP





Hot-gas desulfurization with DSRP.