Status-quo of Technological Development of CCS in China's Cement Industry

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Agenda

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2 Comparison of various methods of CO_2 purification and economical efficiency

3 Main technological routes of CO_2 separation and purification for cement plants

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I. Historical background

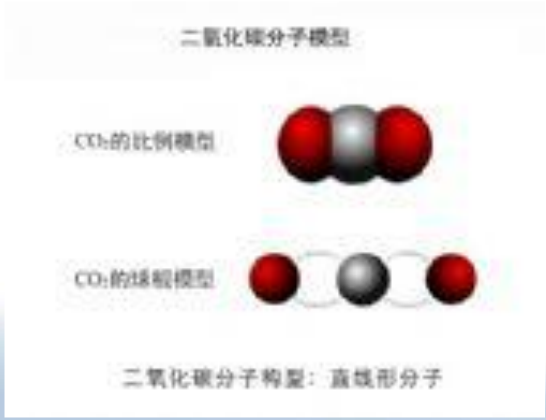
China's energy consumption and CO_2 emissions are growing year by year, which is predicted to increase to 23.9% in 2020, resulting in serious effects on climate and ecology.

The global CO_2 emissions from fossil fuels amounts to 200 million tons annually, accounting for 82% of the total greenhouse gases.

As for a 5000t/d cement plant, the absolute CO_2 emission is 1.5 million tons/y, among which comburents account for 950,000 tons/y, and fuels account for 540,000 tons/y, equivalent to 832 tons of CO_2 emission per ton of clinker and 785 tons of CO_2 emission per ton of cement

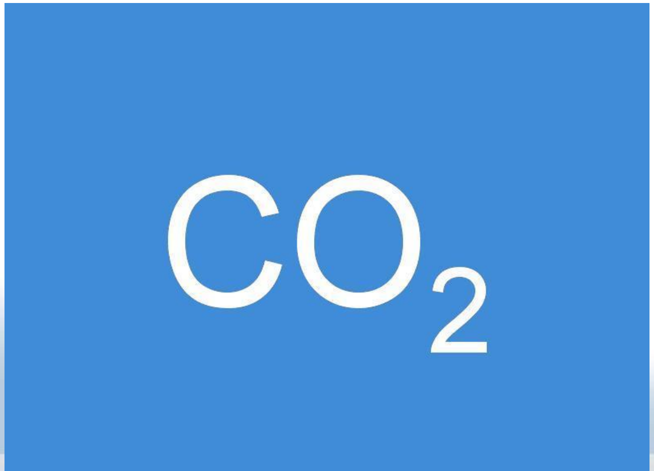
It can be roughly predicted that China's total cement production will reach more than 7.1 billion tons during 2008 - 2012, which would emit about 5.5 billion tons of CO_2, and other GHGs making a great impact on the environment.

According to the International Energy Agency (IEA), if decisive actions are not taken, energy-related CO_2 emission will increase by 130% in 2050 from 2005. CCS is a key technology to reduce CO_2 emission in large consumers of fossil fuels. According to the technology roadmap outlined by IEA, global CCS facilities are expected to capture more than 10 billion tons of CO_2 in 2050, and storage 145 billion tons cumulatively between 2010-2050. To achieve this goal, over 3000 CCS projects need to be built by 2050.



The executive meeting of the State Council held on November 25, 2009 made the decision that China's CO_2 emissions per unit of GDP should be reduced by 40% to 45% in 2020 from 2005. To achieve this goal, we should control CO_2 emissions from cement kilns. China's cement industry is a large CO_2 emitter, of which the potential of CO_2 emission reduction deserves more attention, as this industry not only discharge greenhouse gases (e.g. CO_2) directly from calcining limestone and burning coal, but also indirectly leads to CO_2 emission by consuming electricity and other matters.

Assuming that China's GDP increases at the average rate of 7.5%, based on the current cement production status, it can be roughly predicted that the total cement production during 2008-2012 will reach over 7.1 billion tons. This not only lays heavy burden on resources and energy, but also results in a severe impact on the environment with the corresponding 5.5 billion tons of GHG emissions (e.g. CO_2) based on the current CO_2 emission volume in cement industry. Therefore, to effectively separate and capture CO_2 in the exhaust from cement factories is a crucial issue to be tackled.



Development of CCS in other industries in China

Huaneng Beijing Thermal Power Plant

The plant has the first CO_2 capture and processing system of coal-fired power plant in China, which was started on December 26, 2007 and put into use on July 15, 2008. It covers an area of 500m^2, with a total investment of 28 million RMB, equipment utilization rate of 6000 hours per year and the designed production capacity of 3,000 tons per year.

Huaneng Beijing Thermal Power Plant

Jinzhou Liulu Petroleum Co. Ltd

Gas source: Hydrogen exhaust

Production scale: 30,000 tons

Usage of products: food grade

China Sanjiang Fine Chemicals Company Limited

Gas source: ethylene oxide gas

Production scale: 30,000 tons

Usage of products: food grade

Huaneng Shanghai Shidongkou Power Plant

The project was designed by Xi'an Thermal Power Research Institute, which was started in July 2009 and completed by the end of the year. It is the largest CCS project of coal-fired power plant in the world, which is expected to capture 100,000 tons of CO_2.

CCS Model in Cement Industry—Inner Mongolia Mengxi Cement Co., Ltd

The company, in cooperation with **Changchun Institute of Applied Chemistry** of Chinese Academy of Sciences, has built China's first large-scale CO_2 polymer production line.

The project extracts CO_2 from the cement kiln exhaust and makes it into **food-grade purity** as a raw material for degradable plastics. The annual output is 3,000 tons, which is the largest operating CO_2 polymer production line in the world.

II. Comparison of various CO_2 separation and purification methods, theories and economic efficiency

Types of method	Theory	Advantage (Characteristics)	Disadvantage	Cost
Adsorption-distillation method	Develop and use solid composite adsorbents of special formula to absorb heavy impurities (e.g. sulphide, nitrogen oxides, oxygen-containing organic compounds, various types of light hydrocarbons, carbide and water) from CO_2 step by step, and burn the impurities in the fire (this process would not pollute the air). After that, adopt heat pump distillation technology to separate light impurities to further improve CO_2 concentration to above 99.996%, which could then be used as a product.	The process and conditions are simple and easy to operate, with energy consumption 60% lower than other methods and cost reduced by about 62%. Over 90% CO_2 can be recycled, and the CO_2 concentration of the products exceeds the national food-grade standards resulting in high profits.	1. Adsorption at room temperature and distillation at low temperature and medium pressure 2. Applies to such industries as petroleum, chemical and wine industries, with CO_2 concentration of 80-90%.	Cost: 80-230 yuan/ton
Chemical absorption method	Also called chemical solvent absorption method, with solvent including alcohol amine and ammonia gas (or ammonia water), primary alcohol amine (e.g. MEA), the secondary alcohol amine (e.g. DEA and DIPA) and tertiary alcohol amine (e.g. MDEA). Use solvent to absorb CO_2 to form stable carbamate and then adopt heating method to separate out CO_2.	MDEA has good thermal stability and resistant to degradation. The solvent is not volatile and the solution has weak corrosivity against carbon steel equipment. The technology is mature and easy to operate, and has relatively low requirements on workers, which is a preferred one.	If inappropriate solvent is selected, after it absorbs CO2 and generates stable carbamate, it will result in much reaction heat, and it is hard to regenerate by heating while consuming more steam.	Cost: 300-400 yuan/ton
Membrane separation method	The membrane separation method makes use of a film made of certain polymeric materials which has different permeability in terms of various types of gas. Pressure difference is the driving force of this method: when there is difference in pressures between the two sides of the film, the gas component with high permeability will go through the film at a high rate, while most of the gas with low permeability will remain as residual airflow in the inflowing side. In this way, two gas	The facilities for this method are simple and need less investment than solvent absorption method.	It is appropriate for removing CO2 from natural gas and oil exploration; low heat resistance with upper limitation of 150 ℃ ; difficult to achieve high concentration of CO_2	

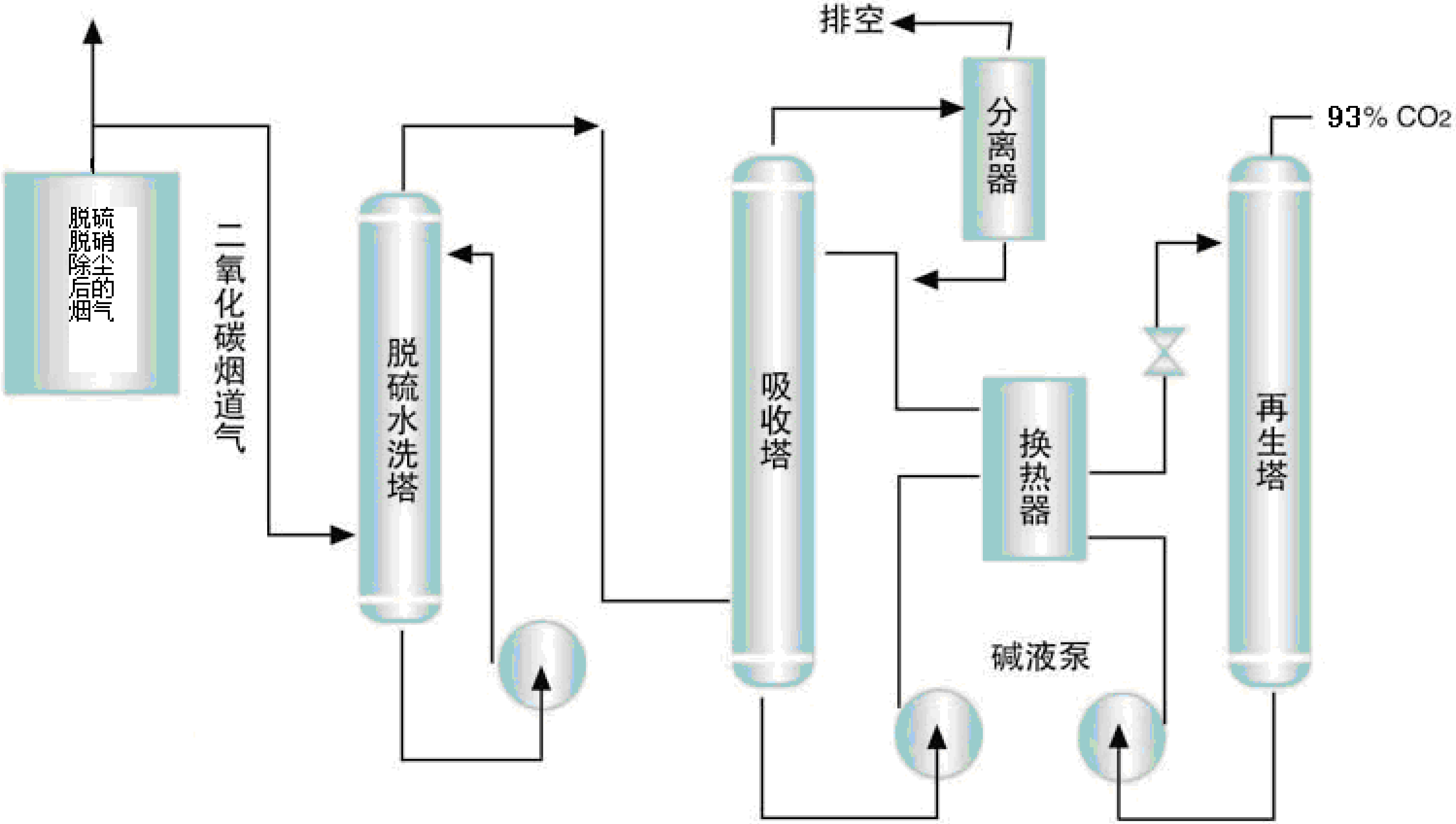
Comparison of CO_2 concentration between cement industry and other industries

Industrial source of CO_2	CO_2 concentration（%）	Recycling method
Power plant boilers, cement plants and flue gas of steel mills	10～18	Chemical absorption method
Lime kiln, magnesia kiln, transform gas and borax carbon solution exhaust	20～40	Solvent absorption method
Oil gas and food fermentation gas	70～95	Adsorption- distillation method
By-product gas of hydrogen, ammonia decarbonization and ethylene oxide	85～95	Adsorption- distillation method

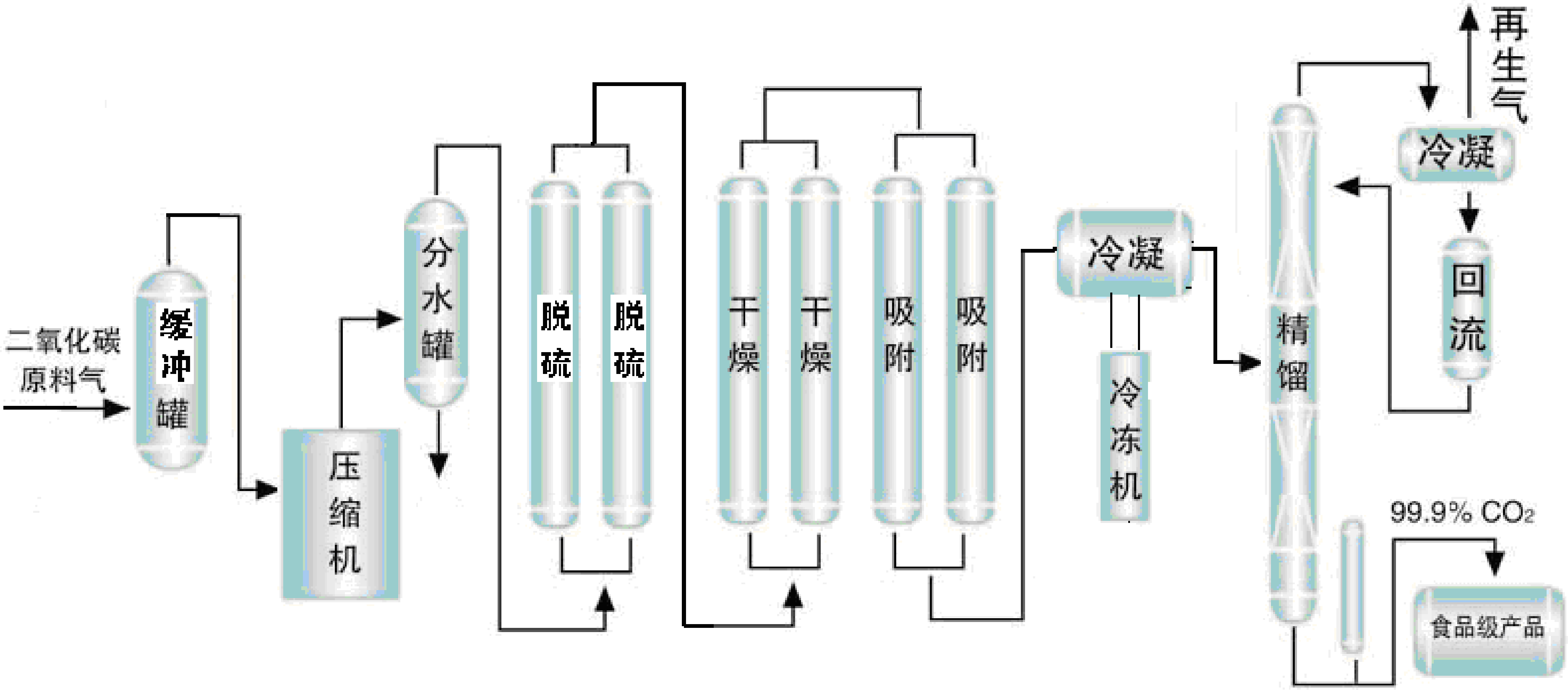
Ⅲ. Technological routes of CO_2 separation and purification for cement plants

3.1、Chemical absorption method + Adsorption-distillation method

❖ 1) The process flow diagram of crude separation by chemical absorption method

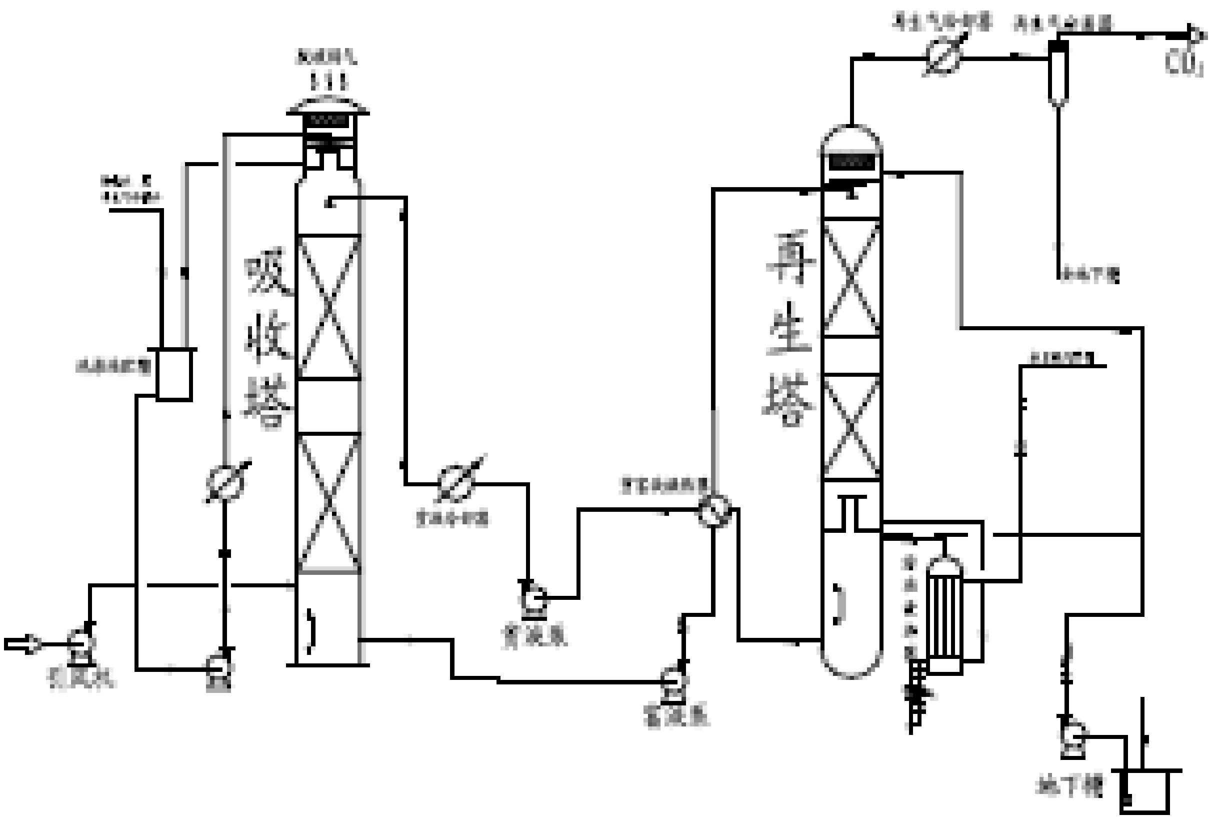


2) The process flow diagram of fine purification by Adsorption-distillation method

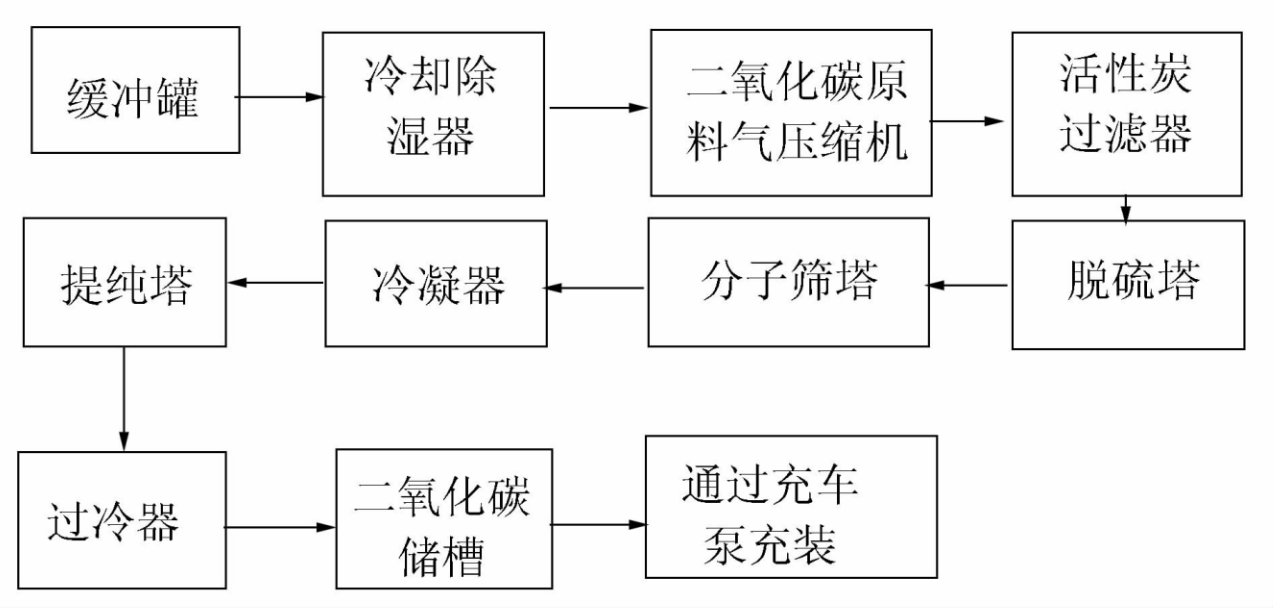


3.2 Chemical absorption method + Refining and purification method

❖1) The process flow diagram of crude separation by chemical absorption method



2) The process flow diagram of fine purification by the Refining and purification method



Example: cement plant of 5000t/d

Thermal parameter of flue gas in the kiln end of cement plant

1、Location: between the bag filter and exhaust fan in the kiln end and the chimney

2、Temperature: 150℃; pressure:1400Pa；

3、Gas component and content：O_2：11~12%；CO_2：17%；CO：150ppm；NO：576mg/Nm^3；NO_2:924mg/Nm^3；H_2O：0.063kg/kg dry flue gas ；SO_2:117mg/Nm^3；dust：117mg/Nm^3

4、Standard state flow of gas source：650,000 Nm^3/h

5、Grade and output of products: food-grade, liquid; 100,000 tons/y

Flue gas in the kiln end of cement plant

Desulfurization
Denitrification
Dedusting
Cooling

SO_2<20mg/Nm^3

NO_x<100mg/Nm^3

T <50℃

Dust<30mg/Nm^3

Chemical absorption
Crude separation

CO_2 concentration reaches over 90%

Fine purification method

Food-grade CO_2 with concentration over 99.96%

1. Desulfurization, denitrification, dedusting and cooling of flue gas

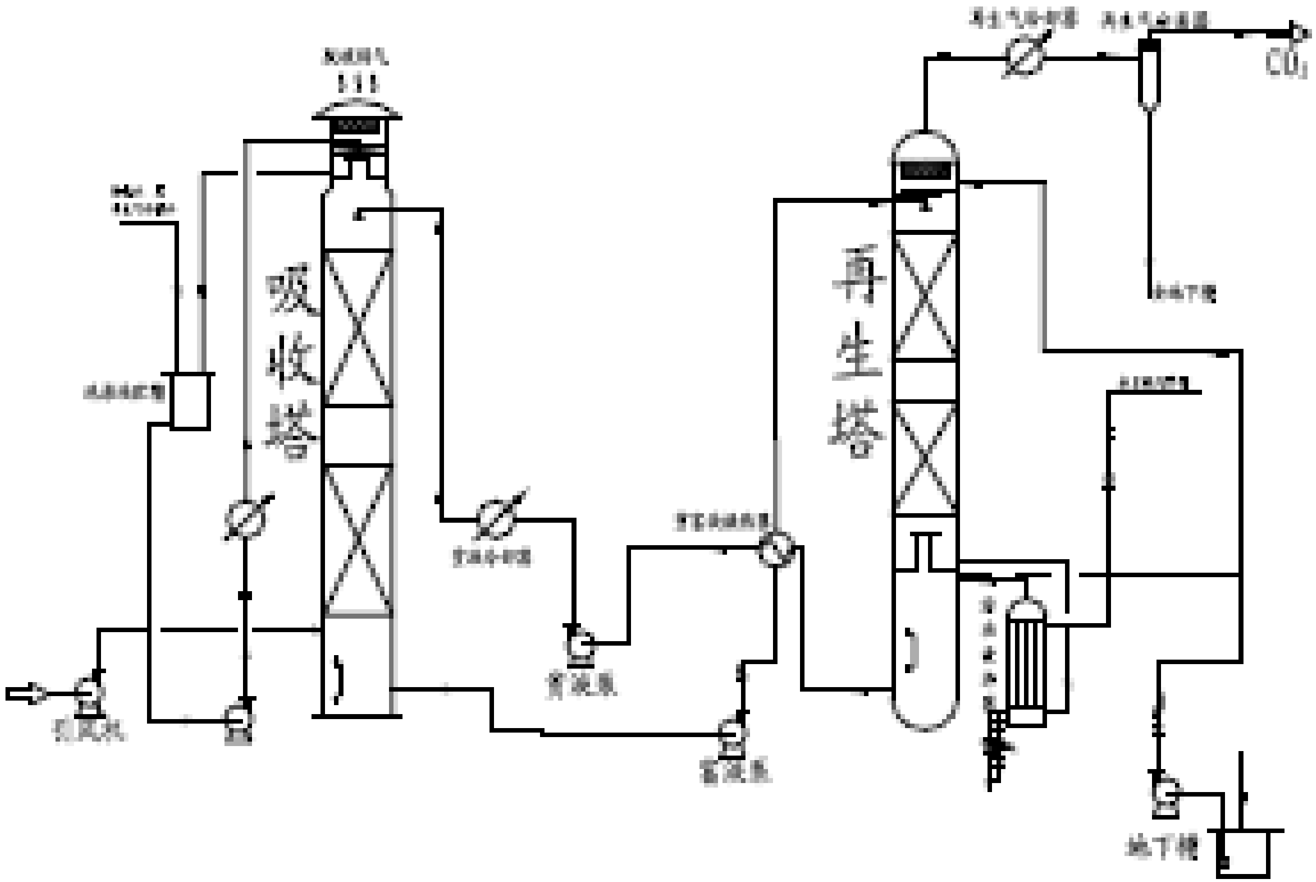
1.1 Wet limestone-gypsum Flue Gas Desulfurization (FGD) process would be adopted for flue gas desulfurization, of which the front-end investment is predicted to about 50 million yuan , with running cost of 1.20 yuan per ton of clinker;

1.2 Air staged combustion technology or SNCR (selective non-catalytic reduction) would be adopted for denitrification, with running costs of 2 yuan per ton clinker;

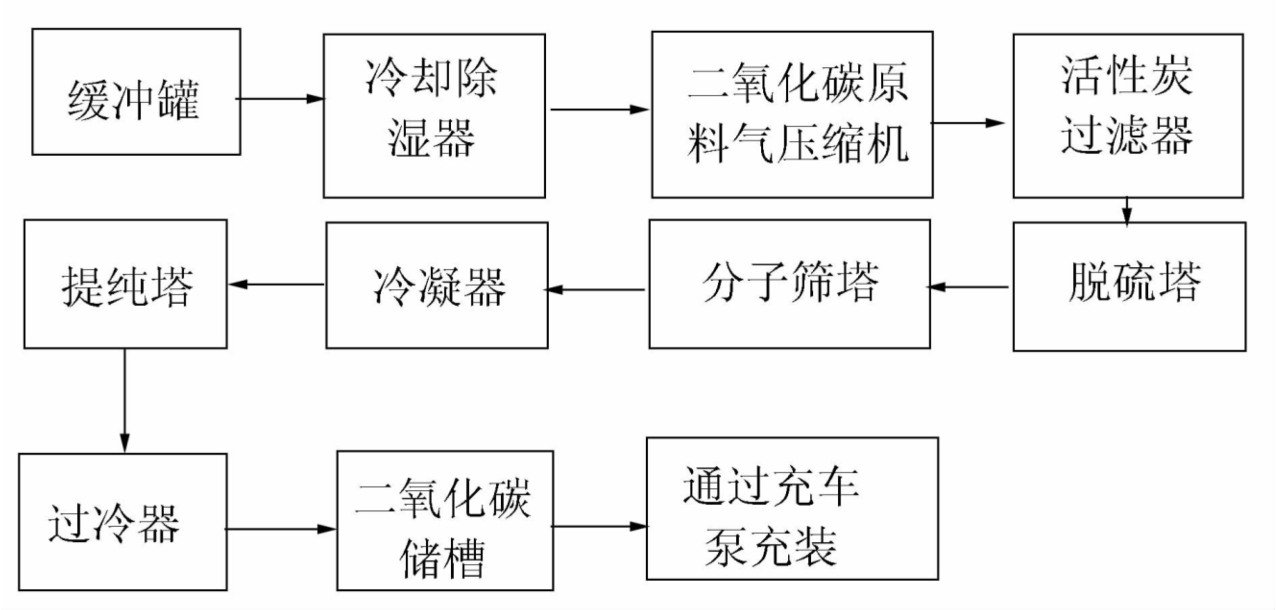
1.3 Dedusting: transforming the (original) kiln end electrostatic precipitator to bag filter, with the concentration of inlet dust <1000mg/Nm^3, the concentration of export emission <30 mg/Nm^3, which needs an investment of 9.5 million

2. Chemical absorption method + Fine purification method (Annual output of CO_2: 100,000 tons)

❖1） The process flow diagram of crude separation by chemical absorption method



2）The process flow diagram of fine purification by the Refining and purification method



3）Designed parameters

Processed raw gas:43290Nm^3/h

CO_2 concentration in gas source: 17％；

Output of CO_2: 12500kg/h；

Annual output of CO_2:100000 tons/y (based on 8000h/y)

CO_2 concentration of capturing system : over 93%

CO_2 concentration of refining system : over 99.99%。

Supplemented serotonin solution:1.5Kg per ton of CO_2

Consumption of electricity : 150KWh per ton of CO_2

4）Running cost

Category and specification		Unit	Quantity	Remarks
Designed scale: CO2		t/h	12.5	
Raw gas		Nm3/h	43900	
Public engineering	Recycled water	t/h	15000	0.2 yuan/t
	Electricity	kwh	44500	0.781 yuan/kwh
	Steam	t/h	167	180 yuan/t
	Fresh water	t/h	330	5.6 yuan/t
单耗定额	Recycled water	t/t clinker	72	14.4
	Electricity	kw/t clinker	214	167.1
	Fresh water	t/t clinker	1.6	9
	steam	t/ t clinker	0.8	144
	Absorption / desulfurization liquid			40
	Dry adsorbent			4.8
	Fine desulfurizer			4.8
Direct cost of workshop		Yuan/t CO2		**480**

Running cost of unit ton of clinker: 28 yuan/t; profit: 30.3 yuan/t

5）Investment estimate

NO.		Cost (10,000 yuan)
1	Desulfurization, denitrification, dedusting and cooling	6000
2	Stereotyping equipment	1900
3	Non-standard equipment	4700
4	Auxiliary engineering	5800
5	Framework of civil engine room, heating and ventilation, purchasing of equipments and spare equipments, freight cost, management fees, working fund, reserve fund, etc.	4000
Total		22400

IV. Technologies for CO_2 resourceful utilization

Carbonated drinks	Adjust taste, restrain and sterilize bacteria, and make drinkers cool	Food-grade, accounting for 70% of domestic consumption, 1000 yuan/t
Food processing	Food freezing, refrigeration, sterilization, mildew-proofing and preservation	Food-grade, accounting for 5% of domestic consumption
Tobacco expanding	Replace freon to improve the permeability, flame resistance and taste of tobacco	Food-grade, accounting for 5% of domestic consumption
Machining	Compared to manual arc welding, CO2 arc welding can improve work efficiency by 1-2 times and save electricity by 50%	Industrial grade, accounting for 6% of domestic consumption, 800 yuan/t
Enhanced oil recovery	Make use of the strong permeability of supercritical CO2 for flooding, to increase crude oil output by 25-38%	Ordinary grade, accounting for 4% of domestic consumption, very promising
Others	Dry ice production, supercritical fluid extraction and chemical production (biodegradable plastics)	Accounting for 10% of domestic consumption, 20,000 yuan/t

CO2 emission from industry

- CO2 emission of industry
- CO2 emission from oil field gas
- CO2 emission from natural gas

Reduce emission by 134 million tons per year

Industrialization of equipments and technologies for capturing CO2 by high gravity technology and resource utilization (distributed, low-cost)

Key technical issue: Distributed CO2 sources

Demands for resource utilization

Increasing oil field output

- EOR needs CO2

Increasing agricultural output

- Gas fertilization needs CO2

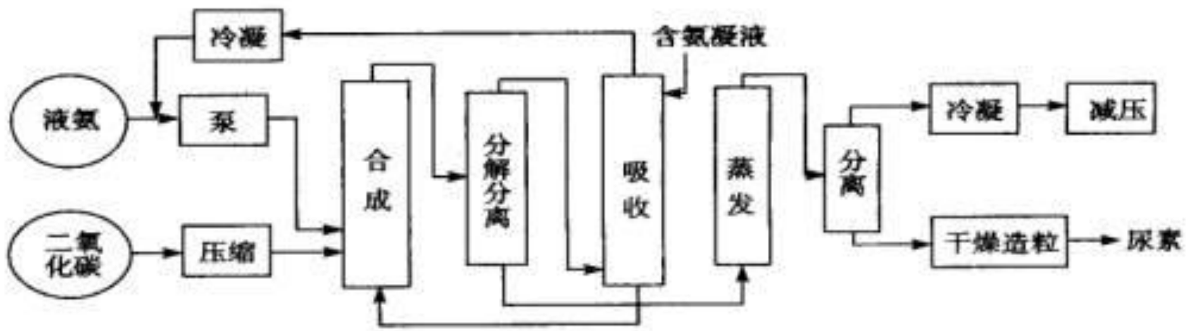
Increase output of crude oil by 10 million tons per year and crop by 150 billion KG per year

CO_2 resourceful utilization

China has developed corresponding recovery methods in terms of various exhaust gas of different CO_2 concentration, including the cryogenic distillation method for oilfield, the membrane separation method for industrialized apparatus of Propylene Recovery, the catalytic combustion method for fine purification, the pressure swing adsorption method in low CO_2 concentration cases, etc.

CO_2 resourceful utilization

Synthesizing urea by CO_2 and ammonia is the most successful model in terms of large-scale fixation and utilization of CO_2. CO_2 can also be used to produce important chemicals (e.g. dimethyl carbonate) with urea, which is an effective carrier for CO_2 utilization. Replacing phosgene with CO_2 to synthesize a series of important and high value-added chemical raw materials (e.g. dimethyl carbonate, isocyanate, methyl methacrylate) can not only achieve clean production, but also make reaction under mild conditions, so as to improve economic efficiency and security of the process.



CO_2 resourceful utilization

The second stage of CO_2 recovery project of Shanghai Petrochemical Investment &Development Co., Ltd has been put into use currently. The project (both of the first and second stage) utilizes CO_2 emitted from ethylene glycol plant, and can produce 75,000 tons of food-grade CO_2 annually, equivalent to recycling 41.25 million cubic meters of CO_2 under normal temperature and pressure annually.

CO_2 resourceful utilization

CO_2-based plastic, e.g. copolymer of CO_2 and epoxides, is also is a hot spot. The plastic is biodegradable, which can help to resolve the "white pollution" issue. China National Offshore Oil Corporation and Inner Mongolia Melic Sea High-Tech Group Company have built two kiloton production lines, of which the industrialization of CO_2-based plastic technology has taken the lead in the world.

CO_2 resourceful utilization

Tianguan Group makes use of self-innovated catalytic system and has built a pilot-scale CO_2 copolymer production line. Guangzhou Institute of Chemistry of Chinese Academy of Sciences has developed the technology of CO_2 copolymer of low molecular weight and put it into production in Taixing, Jiangsu, of which the variety of product is low molecular weight copolymer of CO_2 and epoxides, which can be used as the raw material for polyurethane foam.

Thank you!