Effective CCS System Design Methods Applicable to the Cement Industry

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1. Background
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

I. Historical background

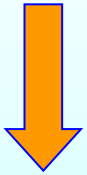
China's energy consumption and CO_2 emissions are growing year by year, which is predicted to increase to 23.9% in 2020, resulting in serious effects on climate and ecology.

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 .emissions.

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.

Hence



- How to effectively separate, capture and recycling CO_2 from cement plant exhaust becomes a burning question

CCS in other industries in China

Beijing Thermal Power Plant of Huaneng Group

The plant built China's first coal-fired power plant carbon capture processing system. The project was started on December 26, 2007, and put into use on July 15, 2008, covers an area of 500m^2, with a total investment of 28 million RMB, equipment utilization rate of 6000 h/y, and the design production capacity of 3,000 tons/y.

Beijing Thermal Power Plant of Huaneng Group

Unit: Liaoning Jinzhou Liulu Petrochemical Company

Gas source: Hydrogen exhaust

Production scale: 30,000 tons

Usage: food grade

Huaneng Group Shidongkou plant

The project, designed by Xi'an Thermal Power Research Institute, was started in July 2009, and completed by the end of the year. With a CO_2 capture capacity expected to be 100,000 tons per year, it's the world's largest coal-fired power plant carbon capture project.

Model of the cement industry on CCS - Mengxi Group

The company, in cooperation with Changchun Institute of Applied Chemistry under the Chinese Academy of Sciences, completed China's first large-scale carbon dioxide polymer production line.

CO_2 extracted from cement kiln exhaust gas is up to the food-grade purity and is used as raw material for the production of degradable plastics. With an annual output of 3000 tons, it's the largest running carbon dioxide polymer production line in the world

II. Comparison of 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	

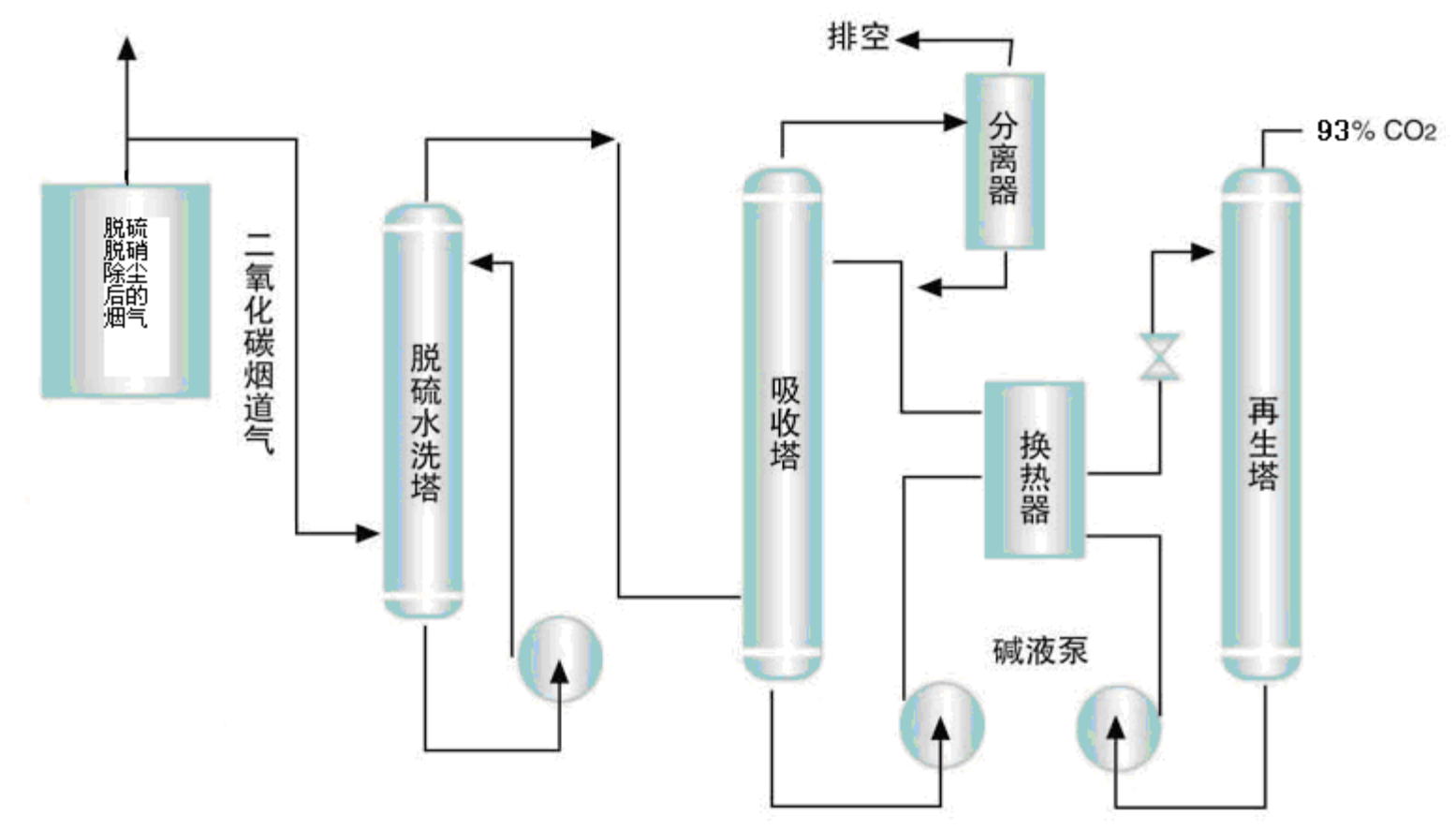
Comparison of CO_2 concentration between cement industry and other industries

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

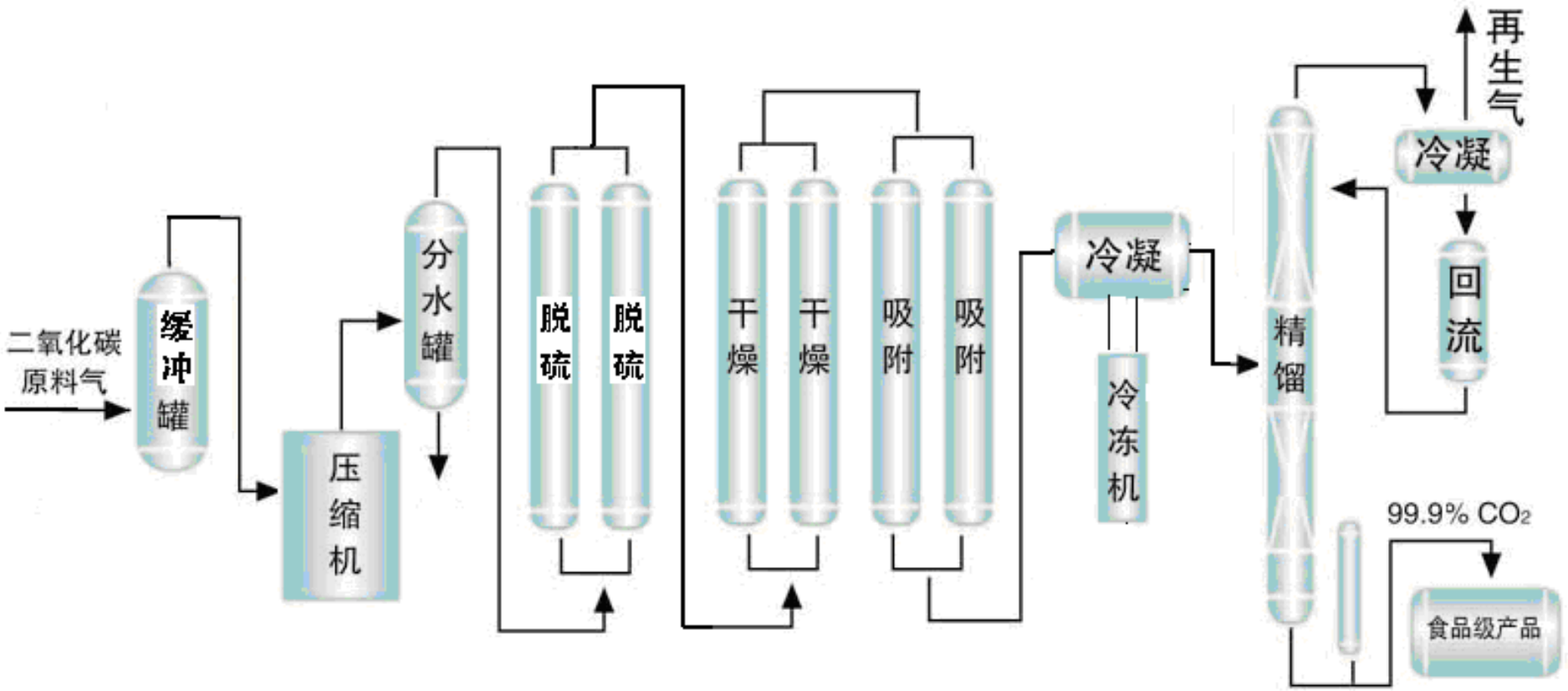
III. Technological routes of CO_2 separation and purification for cement plants

3.1、Chemical absorption method + Adsorption-distillation method

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

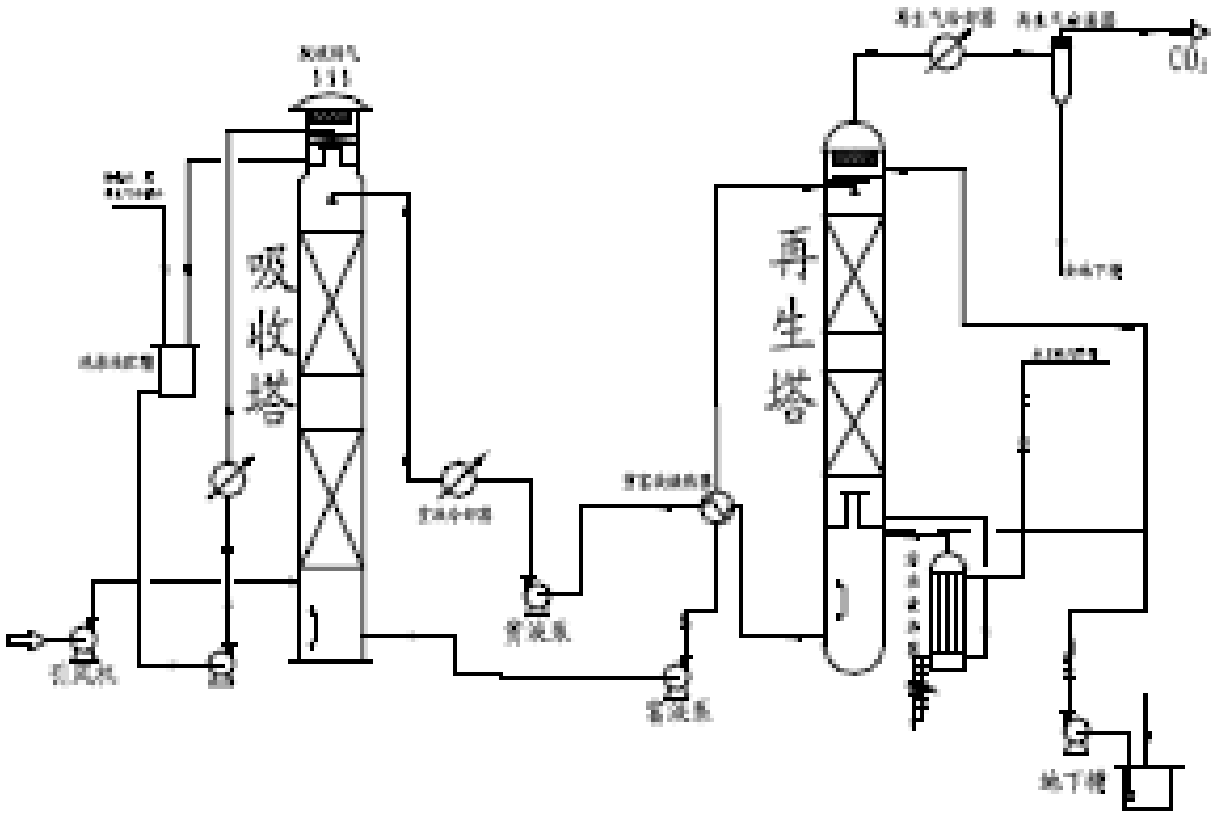


2) The process flow diagram of fine purification by Adsorption-distillation method

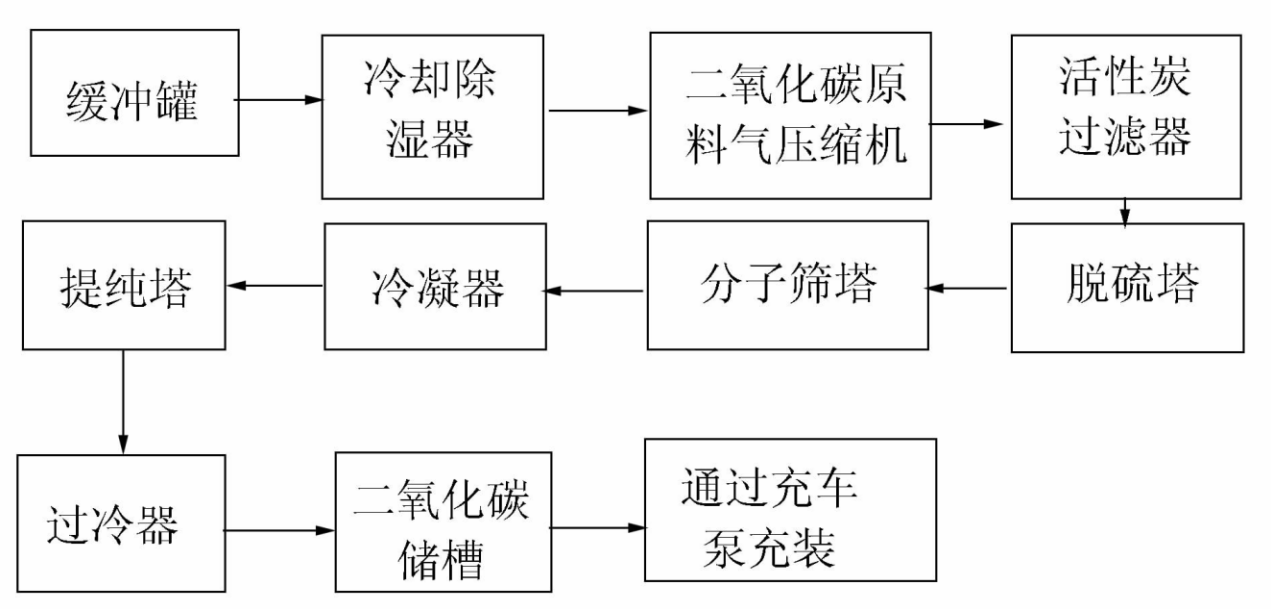


3.2 Chemical absorption method + Refining and purification method

❖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

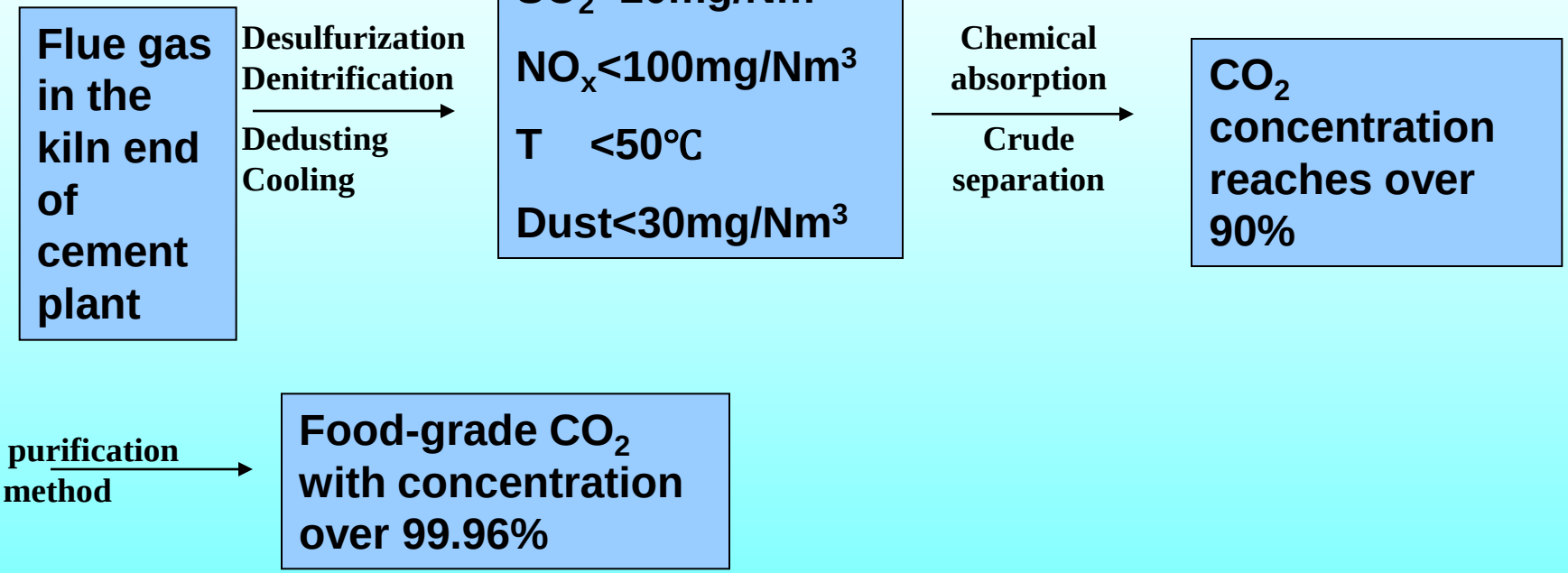
1、Location: between the bag filter and exhaust fan in the kiln end and the chimney

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

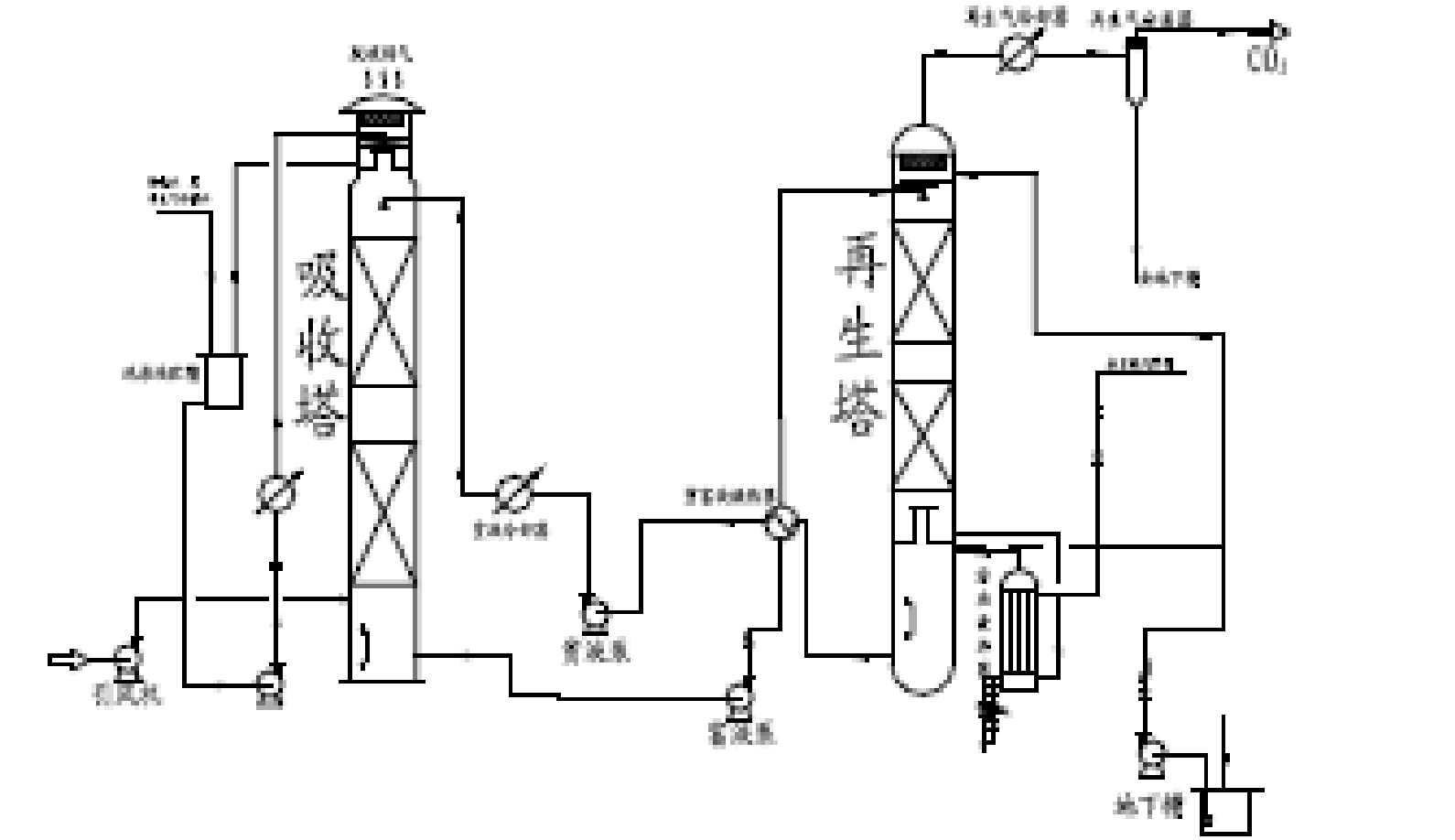
1.1 Wet limestone-gypsum Flue Gas Desulfurization (FGD) process would be adopted for flue gas desulfurization, of which the front-end investment is predicted to about 50 million yuan , with running cost of 1.20 yuan per ton of clinker;

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;

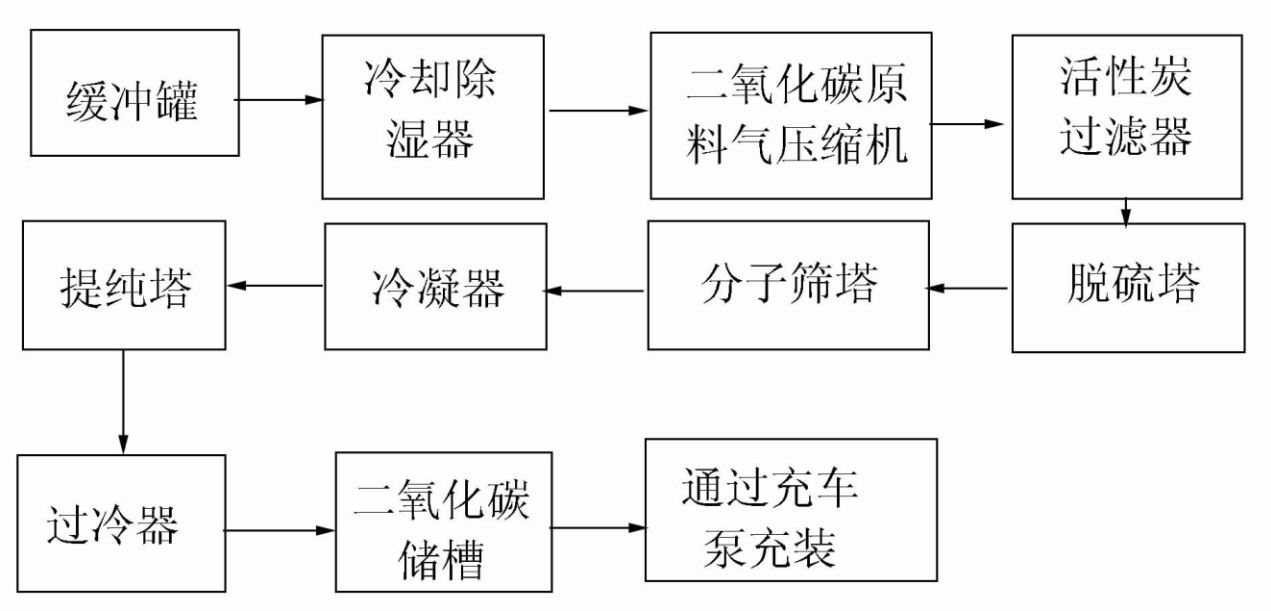
1.3 Dedusting: transforming the (original) kiln end electrostatic precipitator to bag filter, with the concentration of inlet dust <1000mg/Nm^3, the concentration of export emission <30 mg/Nm^3, which needs an investment of 9.5 million

2, Chemical absorption method + refined purification method (CO_2 annual output of 100 thousand tons)

❖1) Process flow diagram of coarse separation by chemical absorption



2) Process flow diagram of fine purification by refined 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: CO_2		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
Unit consumption quota	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 CO_2		**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

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

Thank you!