

Refined New Technology and Its Application Based on the Phosphate Rock Associated Iodine

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ABSTRACT

Iodine associated with phosphate rock is an important part of iodine resources, thus technology development and comprehensive utilization of recycling and refining of iodine associated is significant. From the process of phosphate rock processing recycling $\omega < 95\%$ of the crude iodine need refined into a w of 99.5% or more pure iodine. This paper briefly introduces the phosphate rock associated iodine recycling method, is described in detail sublimation method refining technology and operation method of the iodine analyzes the problems existing in the production and puts forward corresponding solving measures.

INTRODUCTION

Iodine is a world of scarce resources, and its characteristic is low yield, high price, wide uses. Production of iodine is $\square 800$ t/a in our country, but demand of iodine is above 4000 t/a, so demand differences is big, about 80% of the iodine is imported from countries such as Chile, Japan, Turkmenistan [1]. At present iodine in our country mainly rely on extracting from kelp, but iodine yields are low, owing to limited algae production, low technology, large waste of resources and high operating cost factors, it is difficult to meet the basic requirements of iodine in our country. However, phosphate rock in our country contains considerable associated iodine, so much attention are given to development of associated iodine resources and comprehensive utilization of phosphate rock.

RECYCLING OF ASSOCIATED IODINE IN PHOSPHATE ROCK

Associated Iodine in Phosphate Rock

Associated iodine exists in phosphate rock. Zhou Maoji from guizhou geological brigade found that iodine is concentrated in the shallow sea platform margin reef facies and shallow reef near crystal phase within the stromatolite [2], phosphorus are phosphate rock, as well as from the rich iodine of phosphate rock debris within other particles in the structure of phosphate rock facies belt. The content of different iodine of phosphate rock also differ. Iodine in phosphate rock in world is commonly in 0.008~0.013% (ω) [3]. The phosphate rock in guizhou province is abundant in our country, the content of iodine in phosphate rock also ranked among the top nationwide. The content of iodine in sinian system in central guizhou phosphate rock is in general 0.002~0.005% (ω), up to 0.04% (ω). Chemical composition of phosphate mine sample in wengan region are shown in **Table 1** [4].

Table 1. Chemical composition of phosphate mine sample in wengan region.

Ingredient	P ₂ O ₅	CO ₂	Al ₂ O ₃	CaO	MgO	F	SiO ₂	Iodine	Acid Non-Soluble Substance
W%	34.27	5.38	0.26	49.37	1.81	3.11	3.83	0.0087	4.21

Recycling Method of Phosphate Rock Associated Iodine

Recycling of associated iodine in phosphate rock is in the process of phosphate rock, there are mainly two recycling method of thermal process and wet process.

Thermal Process

Thermal process refers to recycling iodine process from furnace gas from ore roasting dressing, the yellow phosphorus process and calcium magnesium phosphate fertilizer production were putted into the high temperature furnace.

Roasting digestion method and chemical method of iodine concentration: Roasting ore dressing is to phosphate rock roasting digestion method, let the impurity carbonate decomposition, and then scrub to remove impurities, reduce the magnesium oxide content in phosphate rock to the scope of wet-process phosphoric acid with mine. Roasting chemical method is to ground phosphate rock in oxidation furnace roasting, oxidation ore after pulp after roasting, carbonation reaction to obtain phosphorus concentration, crystal calcium carbonate solution and regeneration. When roasting temperature reaches 1100°C, iodine began to escape into the gas phase, and then respectively in empty tower (digestion method) or in the condenser (chemical method) to absorb or condensation and crude iodine is obtained. But roasting process is high energy consumption, the method has eliminated, so the iodine method cannot use. In the production of yellow phosphorus and calcium-magnesia phosphate fertilizer recovery of iodine Will phosphate rock and coke, silica according to certain proportion in the furnace or blast furnace melt, iodine and other gases escape in the melting process, furnace gas water absorbing fluoride forms after silicate material liquid, then the recovery of iodine by ion exchange method, iodine recovery rate can reach 70%. But Huang Linchang and calcium-magnesia phosphate fertilizer factory scale is generally small, iodine recycling cost on the high side, fewer production, therefore, yellow phosphorus and recycle iodine calcium-magnesia phosphate fertilizer production enterprises are reluctant to invest.

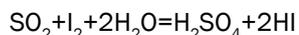
Wet Processes

Wet process refers to extracting iodine from wet-process phosphoric acid production process. Phosphate rock by sulfuric acid extraction of phosphoric acid by wet process, for example, the production process divides two water and half water, domestic multi-purpose water process. A company two water iodine distribution in each phase are shown in **Table 2** [5].

Table 2. Water technology iodine in every phase distribution.

Item	Phosphorite	Phosphoric Acid	Phosphogypsum	Gaseous Phase
Total iodine content W × 10 ⁻⁶	130	60	9	61
Distribution ratio%	100	46	7	47

Recovery of iodine in wet process phosphoric acid process mainly include ion exchange method, air blow out method, solvent extraction method. Ion exchange method, Enrichment of ion exchange method is the most commonly used method. This method is to add acid acidification, by adding antioxidant oxidation into elemental iodine by iodine adsorption, ion exchange column from resin and solvent alkali washing parsing out of iodine, iodine in analytic solution after acidification treatment can precipitate elemental iodine, finally by the isolated from crude iodine, again after the refined substance iodine [6]. Ion exchange method is in recent decades developed a kind of relatively mature and applicable production methods, especially from the recycling of raw materials with low iodine content of iodine. Air blow out method To the raw material liquid chlorine or chlorine water, make the iodine ion oxidized to the free iodine. Material liquid containing a free iodine blow out from the top of the tower spray, contact with the bottom blowing hot air flow, make the iodine by hot air blown out. Blow out general rate was 92~97%. The air containing iodine absorption tower into the upper, absorb sulfur dioxide solution, reductive into hydroiodic acid:



Absorbing liquid of cyclic operation, when iodine concentration of 150 g/L, into the analysis of iodine. Access to disjunctive iodine trap chlorine oxidation, the precipitation of solid iodine, after isolated from crude iodine. Iodine absorption process yield is about 98%. Blow out air method is applicable to raw material liquid containing iodine concentration is higher. Solvent extraction Solvent extraction is a liquid containing iodine, oxidizing agent make the iodine ion in phosphoric acid oxidation for I2 iodine molecules. Iodine is a non-polar molecules, according to the principle of similar miscibility, iodine solubility in the non-polar organic solvents will be significantly greater than in the water solubility. Choose suitable oxidant, extraction solvent, extraction agent, can achieve the purpose of separation and enrichment of iodine. Phosphate rock associated the recovery of iodine extraction technology is constantly improving, industrial application has become increasingly mature. In 2008-2013, urn f group successively completed five sets of wet phosphate rock associated iodine recycling equipment, iodine production capacity of 250 t/a; In October 2014, 50 t KaiLin group also built was put into a wet recovery unit [7]; As the recovery process of dehydration, filtering, removing impurity such as technical difficulties gradually breakthrough [8-10], and VAT group from phosphate rock processing gas phase "captured" associated iodine [11], phosphate rock in our country iodine technology have leading position.

CRUDE IODINE REFINED METHOD

Crude Iodine Refined

On the recovery of iodine in the manufacturing process of phosphate rock, usually the w up less than 95%, short of pure iodine standards promulgated by the state **Tables 3 and 4**, its use value and economic value is less than pure iodine, so must be refined.

Table 5. 100 t/a system the main equipment.

Sequence Number	Equipment Name	Specifications and Models	Count
1	Air compressor	Flow 50 m ³ /h, Pressure 0.8 MPa	1
2	Drying machine	Flow 50 m ³ /h, Pressure 0.8 MPa	2
3	Sublimator	V=1.22 m ³ , t ≤ 200,	2
4	Sublimation machine	Cooling crystallization area 10 m ²	2
5	The sink	V=2 m ³	1
6	Washing circulating pump	Flow 10 m ³ /h, head of delivery 15 m	2
7	Induced draft fan	Flow 2200 m ³ /h, Pressure 0.8 MPa	2

Sublimator

Sublimator is a jacketed ceramic reaction kettle, jacketed medium in is used to heat the crude iodine, and is connected with the external heater cycle heating. There are air hole for import and export, air iodine mixture outlet hole, thermocouple jack and hatch on the roof top of sublimator with insulation cotton and resistant high temperature glass fiber fabric to thermal insulation. Top electric hoist can move for man feeding.

Condenser

Condenser is a framework equipment with surface cooling, fluorine resin cloth were drew along resistant corrosion titanium frame, and it becomes flexible surface formation, cross section was segmented into two square sizes. The framework is divided into downward(main) and upward (auxiliary). The two parts were connected with a funnel to accept a product. There is a hole on the bottom of the funnel, it is used to fill pure iodine, wet iodine or neutral iodine with the container(barrel). The hole was sealed with polymerization bandage under the operating status.

PROBLEMS IN THE CRUDE IODINE REFINED PROCESSING

Pure Iodine Product Quality

The influencing factors on the quality of the pure iodine products mainly are: screening agent selection and dosage, air humidity and operation stability.

Blocker

Can be seen from **Table 3**, the impurity in the crude iodine is mostly water. In addition, there are some F, Cl, Br, SO₄²⁻ and no volatiles, these impurities are handled by a certain blocker, avoid impurities with the gas phase iodine into the condenser and affect the quality of the iodine. Blocker choice depending on the type and content of the impurities to determine the type and quantity. In general, recycled coarse iodine from phosphate rock with alkaline materials as a screening agent. A company blocker in the process of production and the quality of the crude iodine ratio is 0.8~1.5%.

Air Humidity

Experience shows that the air relative humidity is more than 90% will bring sublimation operating difficulties, this is because by air compressor into to the sublimator used for the air bubble into the water, after more than the vapor pressure of water increases, the condensed into water when cooling in the sublimation machine more likely to affect the quality of pure iodine. Air humidity is big, on the one hand, can accelerate the separation of air compressor discharge frequency or increase the air dryer to reduce air moisture to ensure product quality, on the other hand can also add nitrogen in compressed air to solve this problem.

Operation Stability Mainly in the Several Key Links to Control Good Operation Indexes

Such as sublimator heating rate cannot too fast, the system is the water iodine should pay close attention to the quantity of water iodine and the change of pH value, the neutral iodine iodine to speed up the analysis when the frequency and accuracy, and avoid the neutral iodine as a pure iodine finished product packaging.

Productive Rate of Pure Iodine and Yield Iodine

Pure iodine productive rate refers to ratio between a single production of pure iodine yield with crude iodine (100% discount), the general should be around 85%. The main factors influencing the yield as followed: (1) blocker, it shall be determined according to the amount of crude iodine and impurity content, it is in the production practice summary;(2) system to heat up too fast will lead to water is out not completely, iodine steam escape early, appropriate control of heating rate and constant temperature stage is an important part of the guarantee of pure iodine yield;(3) bubbling air amount is too large, the condenser cooling area is not enough, we should pay attention to adjust the dosage of bubbling with compressed air to keep pure iodine production rate.

Yield of iodine is (pure iodine iodine+condensate water iodine iodine in iodine+neutral iodine iodine slag of iodine) and the ratio of crude iodine addition amount, the general should be greater than 98%. Main factors influencing the yield of iodine is as followed: (1) when iodine content id high in tail gas, it should reduce the surface temperature of sublimation, as far as possible when necessary the export section of sublimation four fluorine cloth with forced cooling fan;(2) the bubbling air amount is too

large, so there will be a short staying time within the medium of sublimation, and it affects sublimation effect;(3) gas washing liquid absorbent in the exhaust is to reduce or reduced the volume of circulation, supplement absorbent must be timely, and timely to adjust washing liquid circulation;(4) the system leakage, mostly four fluorine cloth damage or corrosion, should be timely treatment in time.

Tail Gas Treatment

In operation, the temperature stage, or condensed phase, will produce a certain amount of exhaust gas. It is need to use detergents gas absorption (mainly to join Na_2SO_3 or SO_2).

For example of absorption iodine in exhaust using Na_2SO_3 solution:

Tail gas containing iodine from sublimation was imported into the bottom of the exhaust gas scrubber, and contacts with iodine vapor absorption about 5% Na_2SO_3 solution been pumped into the upper part of the scrubber, gas after absorption was let out atmosphere by the exhaust fan. Iodine solution was recycled until after the steam saturation.

Na_2SO_3 concentration in the solution must been controlled in production cycle, usually $\omega\%$ is controlled in 5%~6%, and the iodine content is analyzed of on a regular. When the mass ratio of iodine concentration reached 0.06~0.09% (called a rich fluid), the rich fluid is to remove into iodine recovery system to carry on analysis of iodine. Seen from operation in some company, each producing of 1000 kg pure iodine, it produces roughly 330 kg rich fluid, consumption of Na_2SO_3 is 50 kg.

Fluid clarity must been observed at any time in the production of circulating, if liquid is yellow Na_2SO_3 must been added to ensure normal absorption, to prevent excessive iodine steam discharged into the atmosphere. Auxiliary sublimation could been added after sublimation apparatus, iodine steam been let into the washing system is as little as possible ^[14].

The amount of iodine in the atmosphere environment actually reflects the success of the crude iodine refined. Discharge more, iodine recovery rate is lower, the loss is bigger, the economic benefit is poorer, environmental protection and industrial hygiene conditions are not allowed. The U.S. government industrial hygiene (ACGIH) at the meeting in 1998 working environment the change threshold limit value of chemical regulation: short time contact iodine (chemical abstract registration no. : 7553-56-2) limit is 1 mg/m³. Before standard is formulated in our country, author thinks that the ACGIH provisions can been referred to.

Processing of Condensation Water, Iodine Slag and Saturated Liquid Detergent

Iodine is about 1 g/L in condensation water in the sublimator condenser inner surface. Containing iodine is about 57% (ω) in iodine slag after been refined distillation of completion of the sink in the bottom (mainly sediments from crude iodine, products of blocker reacting with impurities, reagents of blocker reacting with iodine, etc.). Containing iodine tail of gas absorption system of saturated liquid detergent is about 0.06~0.09% (ω), containing iodine in water, slag, liquid must be recycled. Condensed water and washing liquid in Jianfeng company is returned to the Wengfu iodine recycling device in wet process for recycling. Iodine slag is treated with chemical method to recycle iodine.

Equipment Corrosion

Iodine and iodine vapor have strong corrosion and permeability, its corrosion exists in oxidizing, and permeability enhanced oxidation corrosion of equipment ^[15]. Equipment was influenced by high temperature, acid, alkaline and pipeline technology such as high-speed airflow environment in the process of sublimation method refined iodine, it is a complex working environment. Imports section corrosion of sublimator and sublimation machine is most serious for direct contact with the iodine.

Iodine refined devices materials for sublimation method must give priority to the choice of strong corrosion resistance and permeability of iodine. Reaction kettle lined with enamel is used to solve the problem of reaction kettle lining layer corrosion damage in some company. Titanium lined with four fluorine resin was used to sublimation machine imports section and titanium bolts were used to connection of sublimation machine. It does not affect sublimation machine cooling crystallization ability and satisfy vibration and temperature resistant requirements of sublimation import. In the same time it solves the corrosion problem ^[16].

Refined Iodine Granulation

Refined iodine granulation technology is needed to solve. Pure iodine for sublimation method is irregular crystal. Iodine is porous granular in Japan and Chile. Porous granular iodine is convenient to use, so the domestic customers especially pharmaceutical industry has been accustomed to the granular iodine. At present, Guizhou University collaborated with Wengfu are researching and developing iodine granulation technology.

CONCLUSION

As the phosphate rock associated iodine recovery technology is mature and used widely gradually, crude iodine refined is increasingly important. New technology of sublimation method refined iodine will be more and more application. More than 99.99% (ω) of high purity pure iodine has been batch produced already in Wengfu Jianfeng company, because they constantly improve the technology and equipment ^[17], we believe that the recovery of iodine due to refining technology innovation and improvement will boost iodine element industry development in our country.

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