

Khazar University

***School of Engineering and
Applied Science***

***Purification of Industrial waste gases
From Hydrogen sulfide &
sulfur dioxide***

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INTRODUCTION

Purification of industries gases from hydrogen sulphide H_2S and sulphur dioxide SO_2 has great significant and technical interest in solving of ecological problems.

This problem demands solving in industry of petrol producing Countries and petrol chemistry industries.

In process of Cracking of petrol much hydrogen sulphide H_2S is Separated, but such Separation of hydrogen Sulphide and Sulphur dioxide is very dangerous for surrounding.

To prevent hydrogen sulphide and sulphur dioxide environmental pollutants, it is necessary to destroy hydrogen sulphide to sulphur S and hydrogen H_2 .

To-day the wide used method is "Clous" process. But south Countries it is not acceptable because such technology demand big amount of water energy in this process.

That is why this method is not economically acceptable.

To improve technology of purification of petrol chemistry industries gases from hydrogen sulphide H_2S and sulphur dioxide SO_2 .

We Suggested very simple and economical acceptable method

based on electrochemical destruction of hydrogen sulphide till hydrogen and sulphur.

In the electrochemical process in presence of chlorine and other Halogen, sulphur oxide is transferred to sulphate compound. Scientific novelty of this dissertation is next. First it has been suggested electrochemical method of destruction of hydrogen sulphide H_2S and Conversion sulphur dioxide SO_2 in petrochemical industries waste gases.

We have shown the possibility of Conjugation of chemical and electrochemical reactions in destruction of hydrogen sulphide and Sulphur dioxide.

We have developed the technological scheme of hydrogen sulphide and sulphur dioxide.

**CHAPTER 1. THE INDUSTRIAL METHODS OF
PURIFICATION ^{of} WASTE GASES FROM HYDROGEN
SULPHIDE AND SULPHUR DIOXIDE**

(Literature Review)

Purification methods of industrial waste gases from industrial gases which is giving great damage on surrounding.

1.1 - problems of purification:

This problem has two aspects - first aspect connected with treatment of sulphide containing mineral sulphides.

It is meant that part of minerals in the process of oxidation gives very big amount of sulphur oxide which increases damage in nature. For example such damage in surrounding was observed in Canada as result of SO₂ Separation in Washington (U.S.A).

For one day the Separation sulphur dioxide SO₂ from waste gases in Washington gave 42000 U.S. Dollars damage in surrounding of Canada. It means That Pollution of air of one Country influences on surrounding neighbor countries.

In this cases it is very necessary to clear sulphur containing minerals. The Purification of waste industrial gases , from

Sulphurdioxide SO_2 in such cases has big meaning.

It has been shown that amount of sulphur as follows:

	amount of sulphur(IV) ⁴ %	amount of SO_2 %
Coal	1	0.06
	4	0.24
	2	0.12
Mazot	5	0.31

But general amount of sulphur dioxide is very big in waste gases thermalelectric stations. the electric stations with capacity 1000 MKW which use every day 9000 tons coals, containiny 2% sulphur gave about 360 tons sulphur dioxide [1, 2] .

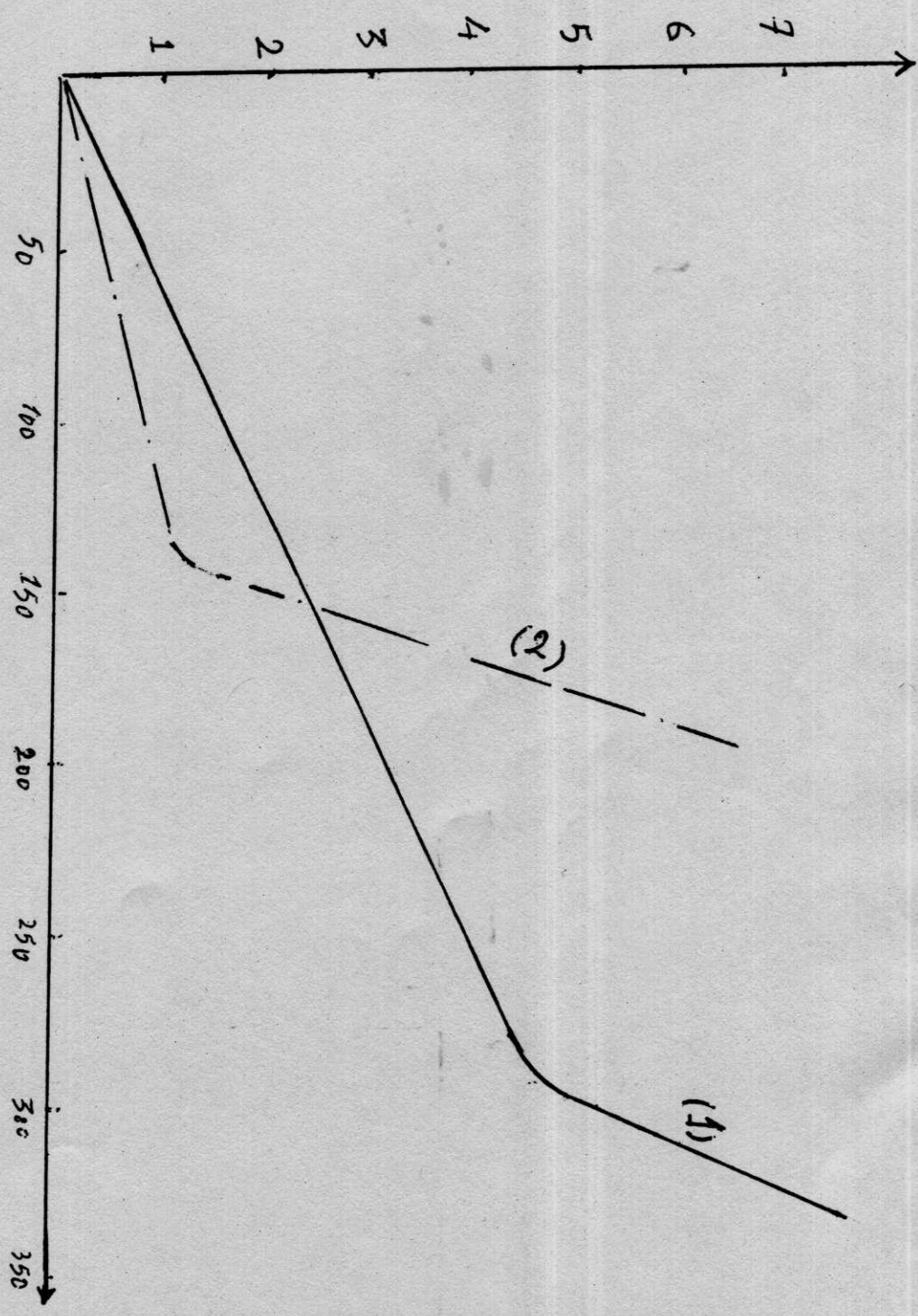
In many cases it has been attempted to treat So big amount of thermalelectro station waste gases.

Some process of treatment are on the boundary of industrial application. The absorption of sulphur dioxide from industrial gases carried out with different methods successfully.

The sulphur dioxide is soluble very little in water but its solubility in alkaline solution is very big.

For clearing it has been applicated the ammonia solutions (NH_4OH) , xylene solutions or methyl aniline, and other ammonia compounds [3]. In sulphidin firm process, as good absorbant is mixture of water with xylene (1/1). After this seprated the sorpted sulphur oxide can be used for preparation of sulphuric acid. It has been tested also toluene, but without of success. Xylene and water usually is not mixturing, but in interaction of SO_2 with xylene some amount of xylene sulphate is formed - when concentration of SO_2 is about 100kg the mixture is become homogenous. In the picture 1-1 was given curve of equilibirity SO_2 - xylene- water system, for the sorption. It is added to mixture solution sodium carbonate and xylene sulphate is transfered to sodium sulphate , but SO_2 is directed to stripping column in 95-100c°. The mixture of sulphur oxide (IV) containing very little amount of xylene is washing with water and produce pure SO_2 , for recooperation of xylene vapour from waste gases it has been used diluted sulphuric acid.

Absorption of SO₂ %
by volume

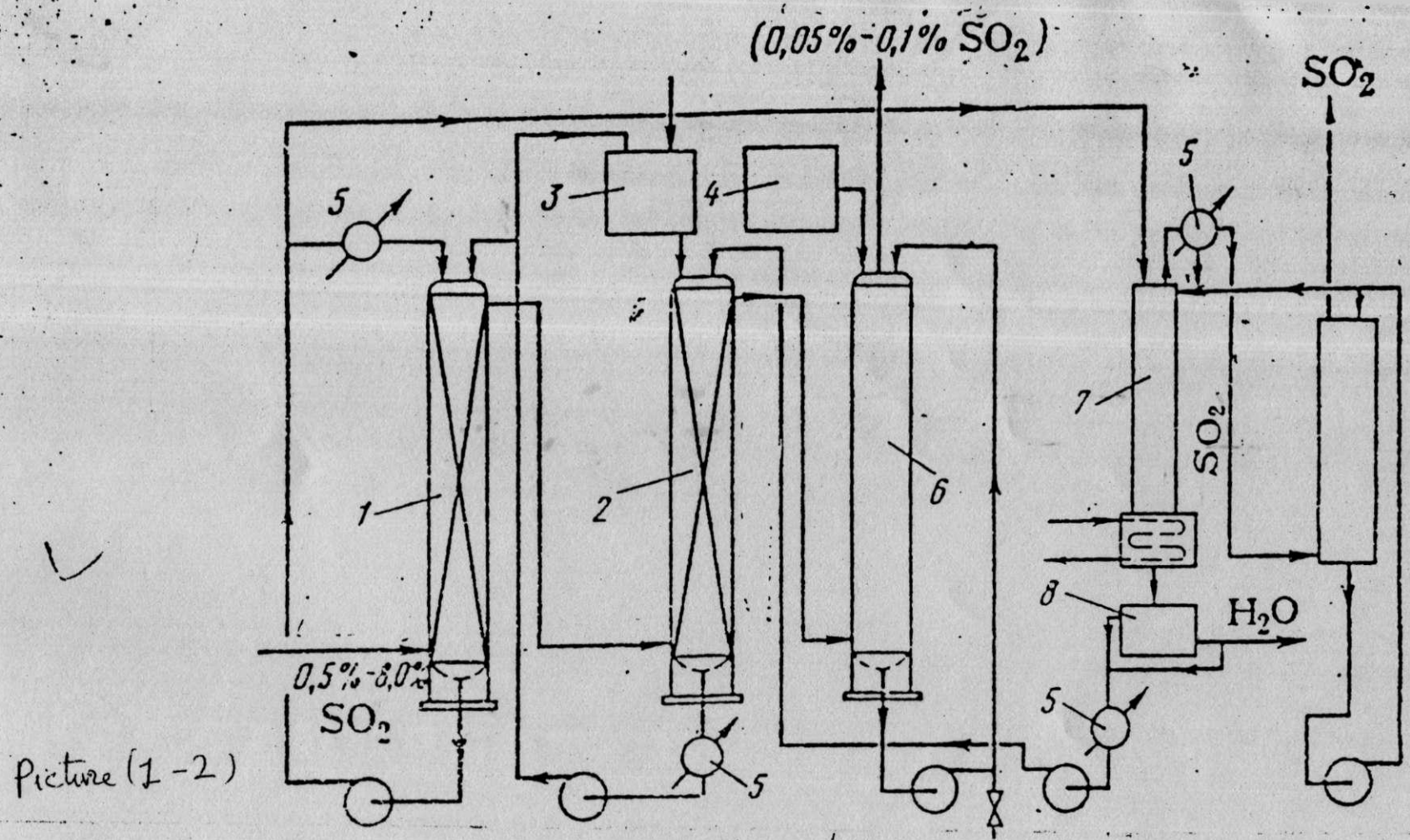


Picture 1.1 concentration of SO₂ in Kg/M³ t° 23-25 c°

Iso therms of SO_2 absorption with dimethylaniline without of water (1) and with mixture 1:1 water- xylene (2) showed that absorption takes place more effectively in temperature 150 [4].

In beginning of process SO_2 concentration was 8% , after scrubber it is lowered to (0.05-1)%

In low concentration it is become uneconomical because lost of xylene. technological scheme is given in the picture 1.2 picture 1.2 describe technology scheme of SO_2 absorption with mixture xylene - water [5].



Picture (1-2)

Picture (1-2) Technological schem - SO₂ absorption with mixture xylene- water [455]

- 1.2 - absorption column 3 - tank of solution (calcinatin- soda) 4 -tank of diluted H₂SO₄ 3 - Refrigerated solution
- 6 - washing column 7 - stripping column 8 - separator

This process developed by American smelting refining Corporation. SO_2 is absorbed with dimethyl-aniline, separated in desorption of sulphur dioxide also is differed with high purity [4].

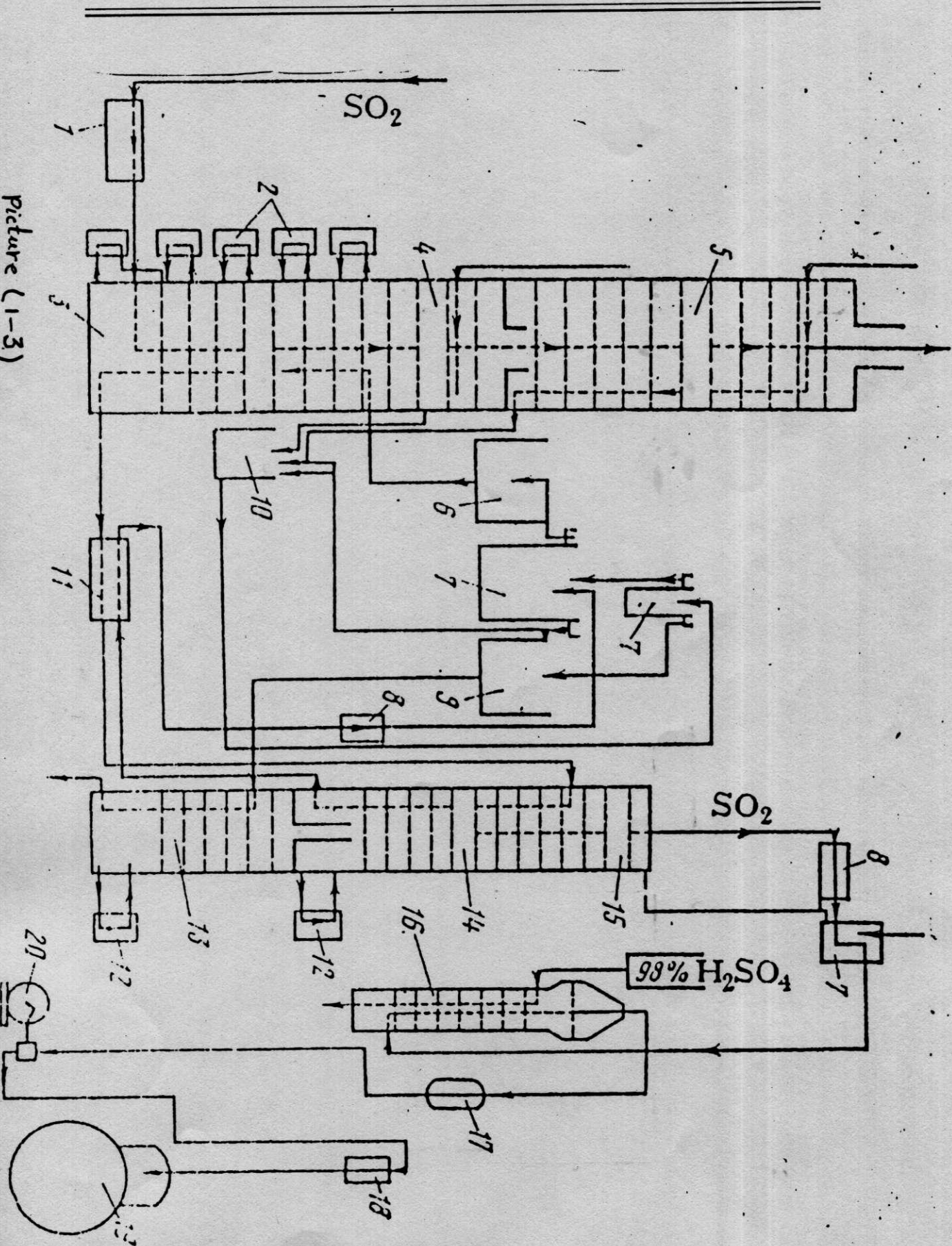
First, gas is passed via electrofilters and hard mixtures is moving away and is washing with pure methylaniline. From diagram 1.1 it has been seen the concentration SO_2 is more 3.5%. The dimethylaniline is more effective absorbant than the mixture of xylene-water economically and more useful. Gases containing is washing with solution of sodium carbonate for moving away little amount of SO_2 and dimethylaniline. Enriched with SO_2 solution is going to stripping column via is steamed with SO_2 . Gases are going to scrubber for reoperation of methylaniline after to dried tower for moving away wet and directed to inventory for using SO_2 . Plant Constructed in Selbi (California) with capacity 20 tons day. SO_2 is reopering 90% of sulphur dioxide from waste gases. for 1 kg is separated sulphur dioxide is spending 0.5 gr dimethylaniline, 16 gr sodium carbonate and 18 gr sulphuric acid also 1 kg water vapour, 0.52 MJ energy and 8.2 kg/h cooled water. technological scheme of the process is giving on



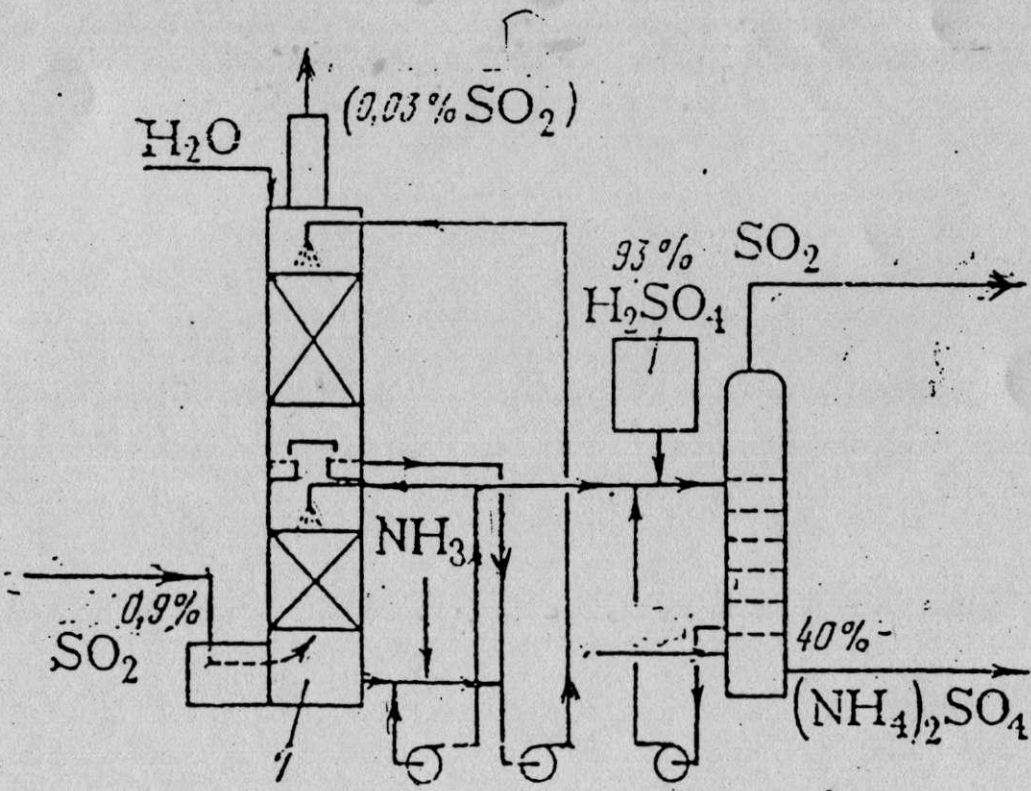
picture 1.3. the plant has very low cost.

"consolidated mining and smelting cooperation" in Traille applied ammonia solution as reagent for absorption sulphur dioxide SO_2 . This technology is called Cominco process. the technology Scheme of the Process is given in the picture (1-4).

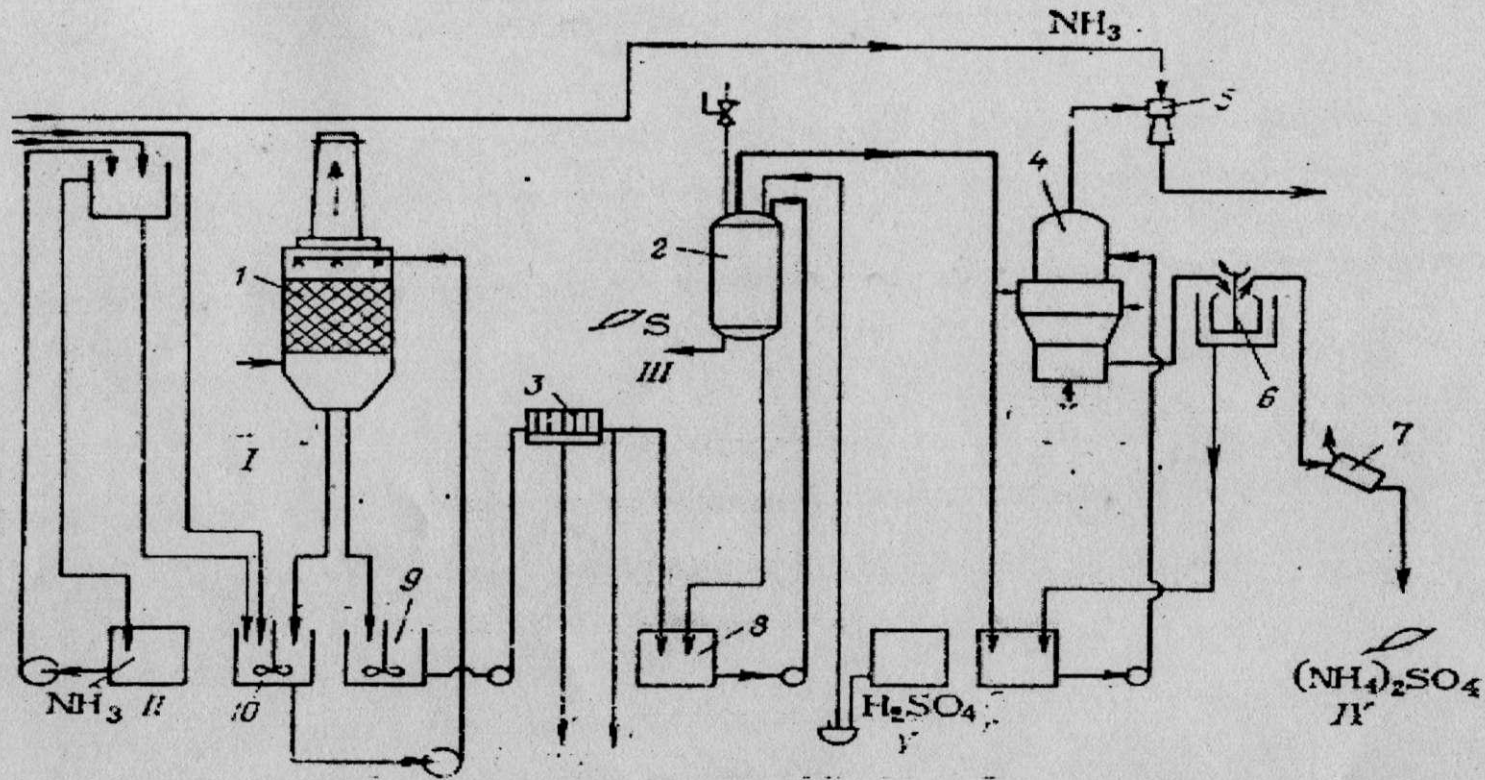
Gases are passed via two steps column with nozzles made from tree. Absorption carried out with mixture of diluted ammonium sulphate solution. The sulphur oxide is separated from ammonia sulphate solution by adding of concentrated sulphuric acid. In this process are preparing SO_2 and $(\text{NH}_4)_2\text{SO}_4$. In next sulphur oxide SO_2 is used for production of acid. process is applied in wide diapazone of concentration (0.1-1.5)% for clearing industrial gases. waste gases are cooled and directed to the layer of activated carbon placed in cylindrical reactor, where the catalytical oxidation of gas and absorption of formed SO_3 with water takes place. prepared acids is washing from reacton and. concentraiting till 65% with using of heat of gases.



Picture (1-3)



Picture (1-4) - Technological scheme of Cominco process



Picture 1-5 Processes of Simon – Karvez absorbtion of SO_2 by ammonium and washing with cock

1-Scrubher; 2-Autoclave; 3-Pressure filter; 4-Vaccum; 5-Injector; 6-Centrifug; 7-Dryer; 8-Tank; 9-Tank of scrub solution; 10-Circulation Solution tank

I-Purified gas; II-Ammonium solution; III-Sulphur; IV-Crystalline ammonium sulphate; V-77% H_2SO_4 .

The effectivity of reoperation is about 95% and concentration SO_2 in going out gases not little than the 75×10^{-6} mol/li, in beginning Concentration of gas was 1.5%.

Moving away sulphur oxide from industrial gases more complex because of huge amount of low concentrated of purified gas. But the process didnot confirm the mechanism of purification based on using of pure water. usual river water cannot be used for wet purification of gases, but temza river water having alkali reaction was used for washing gases of thermal electric stations in Bathric and Benside. But this process is limited because of scrubber increases in the river waters the concentration of calcium sulphate CaSO_4 , the last helps the formation scum in heat exchange, and also influence on the river flora and fauna.

Besides, so industrial gases after of scrubber have low temperature and residue sulphide oxide dont dispersed on the big square, creat high local pollution. Absorption tower made from iron-cast with internal covered with tree wood. Sea waters has been used sucessfully for clearing waste gases from zinc sulphide plant.

(From electrical zinc corporation Rith down Australia), tower with tree nozzles with square 12.1 m^2 , diameter 5 m height 5 m, treated $85000 \text{ m}^3/\text{h}$ gas, containing 5% sulphure oxide in temprature $180\text{-}200^\circ\text{c}$ In experimental scrubber with limited on spending water, this plant has effectivity more 95%. In last variant of the plant capacity is $8000 \text{ m}^3/\text{h}$ gas, Spending of water is $3.25 \times 10^6 \text{ kg/h}$. scrubber have electrofilter for absorption of fog, that allow to low concentration of So_2 from with 22% till 2×10^{-6} . In lowering of limited spending waters effectivness of clearing is also lowering and concentration So_2 in waste gases is increasing till to more 30×10^{-6} Bromly and Rid [6] carried out investigation on the experimental plant of wet clearing of gases containing So_2 with sea waters. Relation of liquid and gas is about 25 kg sea waters ands more 1 kg gas. Effectivness of clearaing on one stage is 90% . Effectivness of clearing is 99% and, more . In result of oxidation of soluble sulphur oxide is transfered to sodium sulphate, which can be used in the plant for solubility of So_2 . sulphuric acid is added for prevention of scum formation. volume of sea waters can be decrease in five time in application more complex

absorption apparatus.

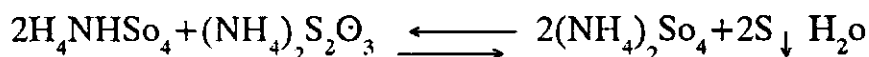
for example many stage plate scrub with boiled layer have been used. PH of prepared solution is between 2 and 3, if this solution goes to sea it is necessary to neutralized it with calcium hydroxide. this process based on the washing with alkali river water, have developed ICI [7]. Absorption tower is circulating lime solution (5-10)% by mass. In this cases calcium sulphite CaSO_3 is found which is oxidated thiosulphate with oxygen containing industrial gases. technological scheme was given in picture (1-4). Problem of scum formation in super- saturated solution containing calcium sulphate has been prevented by passing of solution via decantator with lime sludge, in which is created necessary PH. Before Solution is directed again to absorption tower, surplus of calcium sulphate was crystalized. part of crystalical sludge was going to volume, in which crystals are moving away. So formed CaSO_4 polluted with volatile ash it cannot be used. It has been suggested to treat it with ammonia carbonate for preparing ammonia sulphate [8] . Japan engineering corporations and Mitsubishi heavy industries has been patented process based on that principals of

ICI process. But in this cases it has the crystals of CaSO_4 were prepared with high purity [9 , 10]

In soviet union also the Suspension of mineral lime are applied for moving away of sulphur oxide SO_2 from industrial gases [11]. stayed concentration of SO_2 in tail gases is lower till 0.15 in million part of sludge. The mixture of sulphite and sulphate was not used for this purposes. other processes carried out in industrial scale. spending of gases is $95000 \text{ m}^3/\text{h}$. this process are the same with Simon-Karvez Process [12-13-14]. Picture (1-5).

Industrial gases are washing with ammomim solution getting from gas plant. to going away gases from scrub solution was added little ammount of sulfuric acid 77% and mixture are staining under the press (1: Mpa , 170 c°, continousness three hours).

In this condition it is prepared sulphur in ammonia sulphate.



Comparing of relation economical effectivity of three used industries processes of wet clearing show that the process of Hoden (ICI) is more cheep. If the river water has good quality or containing

ammonia or ammonia is preparing from gas plant, Ful-Heme - Simon-Karvez process is economically effective.

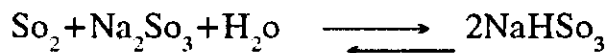
Patelina [15] information about modification of Ful-Heme-Simon karvez process develop in U.S.S.R

Saturated solution of sodium bisulphate NaHSO_3 treat with sulphuric acid and undergoes to the struction in reaction in the 600 KA and 147°C . Effectivness of clearing is 93-97%. Experimental plant with capacity $50000 \text{ m}^3/\text{h}$ constructed in 1986 years.

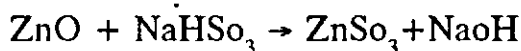
Mitsubishi (heary industries) [16] also developed wet clearing process of gases with using ammonia but in differing from Ful-Heme-Simon karvez process. As result it has been prepared chrystalic phosphate ammonium. the effectivness of moving away sulphure oxide is 95%. Petelina [17] inform also about process magnesium cycle, used in U.S.S.R, for moving away SO_2 from thermal electrostation gases, or from gases whiches are formed from high sulphur content mineing mineral gases. The gases are washing with suspension on magnesium - sulphate (MgSO_4) and magnesium oxide crystals in solution of sodium sulphate. It have been carried out lists on purification on of gases in

agglomeration plant with capacity $800 \text{ m}^3/\text{h}$. It has been found that effectiveness of SO_2 removing is (95-98)% for industrial plants clearing 4×10^6 have been constructed in 1969 Magnitogorsk combined, from SO_3 gases. In other process ammonia as absorbant is using, this process has been developed by Sim-Son and Levis [18]. other possible process is in that industrial gases which react with sodium sulphite and sodium bisulphite Na_2SO_3 , NaHSO_3 .

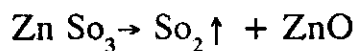
In this process the amount of bisulphite is increasing.



Formed Solution react with zinc oxide.



Zinc sulphite is roasting and, is preparing Zinc oxide and sulphur dioxide SO_2 (IV) which can be used again.

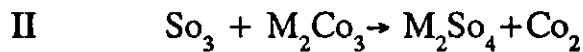
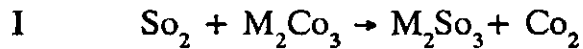


As absorbant it has been used also aluminium sulphite.

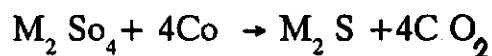
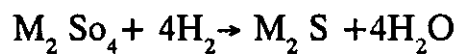
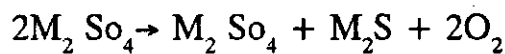
In the process of high temperature wet clearing of gases developed in atom laboratory of from North American Rockwell- Corporation.

Eutectical Point of mixture containing alkali metal carbonate [18,

19] which has $\text{Li}_2 \text{Co}_3$ 33% , $\text{Na}_2 \text{Co}_3$ 35% , $\text{K}_2 \text{Co}_3$ 35% the melting has point 397°C . It is a liquid 425° the density is $2\text{g} / \text{cm}^3$ the process has stages of absorption, reduction and regeneration of absorbant. In process of absorption sulphide oxide containing in gases react with carbonate with formation of sulphite and metal sulphite:

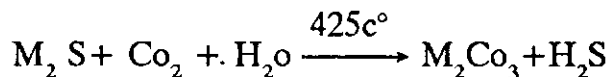


The velocity of reaction is very great. that is why absorption is determine with velocity of sulphur oxide mass transfer. The velocity of washing gas in scrub is 7.5 m/sec . Effectiveness of removing is 95%. In the stage of reduction and generaton gases are using after reforming ($75\% \text{ H}_2$, $21\% \text{ CO}_2$) in temperature 600°C and in condition of reduction reaction of this proportional which takes place.

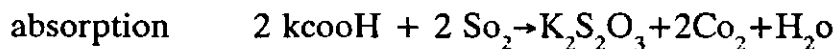


The reduction reaction takes place slowly, the periodical process is longing from 40 till 60 minutes. It has been show that it is more

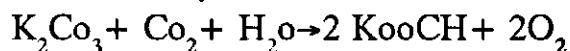
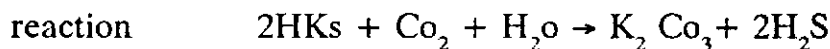
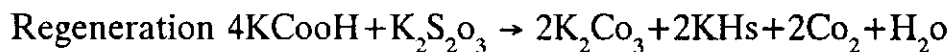
rapidly process. In the regeneration stage sulphites react with mixture CO_2 and water in 425°C



It has been Found that Potassium formate also can be used as absorbant in temperature 177°C [19] , medium effectiveness SO_2 absorption in the beginning of process is 88%, the reaction followed next.



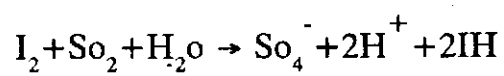
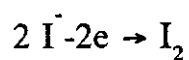
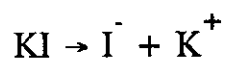
reaction



Shabanov is cowork has developed electrochemical oxidation method of transferring SO_2 to corresponding SO_4^{2-} [20]. In this method based on using iodine solution via which pass industrial gases Containing sulphide oxide in the electrical field.

In this process potassium iodine is electrolysed giving sulphate and iodine ions. Iodine ion is transferring to molecular iodine again. This process has very great economical advantages and simple on

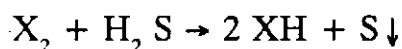
technological scheme. the oxidation process on next reactions takes place:



CHAPTER 2 : PURIFICATION OF INDUSTRIAL WASTE GASES FROM HYDROGEN SULPHIDE

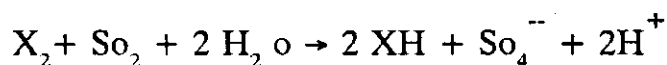
Our method of hydrogen sulphide purification of industrial waste gases based on electrochemical and chemical conversion of hydrogen sulphide H_2S . The novelty of this process is conjugated chemical and electrochemical process.

chemical process followed next: under electrochemical interaction in presence of halogen containing salts it is separated halogen. separated halogen react with hydrogen sulphide in next scheme:



The formed halogen take part in chemical oxidation of hydrogen sulphide again.

The mechanism of conjugation conversion of sulphur oxide to like to hydrogen sulphide electrochemical and chemical oxidation. In electrochemical process the sulphur oxide in presence of halogen salt is converted to sulphate ions.



In connection with mechanism of conjugation electrochemical oxidation with chemical we have studied interaction of chlorine, bromine and iodine salts with hydrogen sulphide under electrical field.

In all cases hydrogen sulphide H_2S is destructed to colloidal sulphur.

We also have shown that chlorine gas very active oxidation agent in this process but chlorine gas very poisoned compound. that is why using of chlorine in this process is not useful because of technological unusfulness. Besides chlorine is not ecologically acceptable.

In presence of chlorine corrosion of metal constructions of plants takes- place.

We also tested bromine alkality salts in our method. Bromine also very dangerous volatile compound. and cause many deases in humam body. It is also cause corrosion of metal construction and ecologically is unacceptable. Next we have studied iodine alkaly salts in conjugated oxidation process of hydrogen sulphide.

Iodine has very interesting properties. It is not dangerous for health and is not volatile in water solution, in presence of sodium and

potassium iodine.

The alkali salts of iodine also undergoes to electrochemical reaction very easily, the voltage of electrolysis is about 0.5 volt. the process of electrochemical oxidation demand very little electricity.

It makes this process technologically acceptable and economically more useful.

The mechanism for electrochemical oxidation process have been studied in analytical chemistry department of Azarbaijan state oil academic by professor shabanov. A.I. patent No [21].

The main clearing methods of waste industrial gases from hydrogen sulphide H_2S have next basic methods:

1 - Physical 2 - chemical 3 - physicochemical 4 - Electrochemical

2.1 - Physical methods of neutralization of hydrogen

sulphide H_2S

In practice clearing of water from soluble hydrogen sulphide H_2S it was applied physical aeration method. Aeration base on contact of water containing soluble gas with air or other gas.

Aeration method is not effective method for removing of

hydrogen sulphide, because of needs to big square and pollution of surrounding. In last years it has been studied application also physical method - vibration a waves.

It also has been used long frequency waves 185-254 nm.

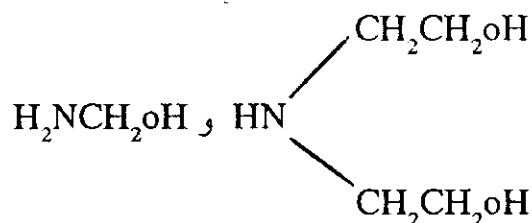
All theses methods didn't find industrial application.

2-2 - *Chemical methods of neutralization hydrogen sulphide.*

All chemical method are divided in two main group:

- 1 - Absorption with liquids
- 2 - Absorption with hot compound

absorption process found more industrial application. The process based on using water solution of mono and diethanol amines



The sorption of acid gases are carried out in heating of absorbant in 115-125°C temprature. Acid gases stimulated corrsion of apparatus, therefore amount of absorbant (amin) is taking 0.5%. Ethanol amin method of clearing allows to decrease of hydrogen- sulphide H_2s

concentration in purified gases till 20 mg/m^3 .

But in using of exceed pressure allows to be carried out more deep clearing. Spending monoethanol amine is 33000 gr/1000m^3 of clearing gas.

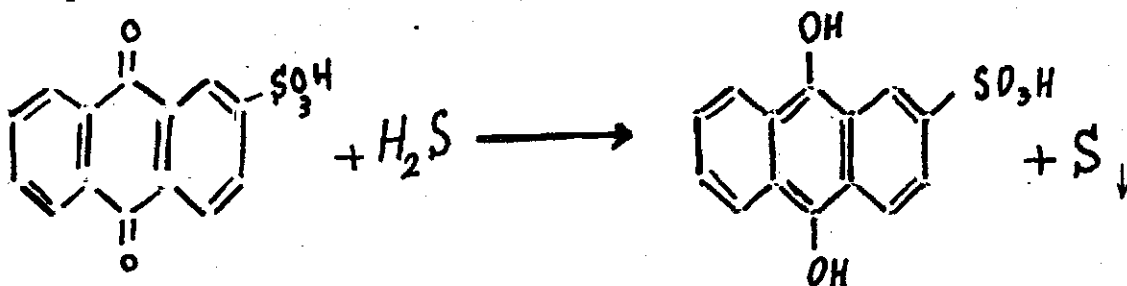
It has been known the arsen- soda method of clearing gases from hydrogen sulphide H_2S which developed 1930-1932 years and widely used in clearing natural, generator and water gases [22]*.

The effectiveness of clearing is (90-98)%. For clearing gases with hydrogen sulphide H_2S concentration 10 gr/m^3 , the amount of arsenic in solution it is necessary to keep 10-20 gr/lit solution alkalinity it is also to keep in known range. Decreasing of alkalinity can give sedimentation of arsenic compound. But increasing can give minor reactions, increasing soda spendings and decreasing sulphur yield. PH of solution keeps 7.85-7.90. As result of minor reaction the density and viscosity of solution increase. Therefore one part of solution systematically is gone out from cycle and neutralize with sulphuric acid. The plant is very huge, for it serving is demanded many persons. In many cases it is necessary additional deep clearing.

Poisonousity of As compound and necessitate of deep clearing of water make this method not acceptable [23]

One of new hydrogen sulphide clearing methods is Stret -Ford method [24] Gas is washing in water solution of alkaly PH (8.5-9.5).

Necessary solution is passing reactor in Period of time for interaction of soluble hydroyen sulphide with O=C group of antrokinosulphonic acid. As result of sulphur separation it is formed corresponding hydroquinone which from reactor is directed to oxidation tower, where in aeration process, hydroquinol oxidized to hydroquinone:



Separated sulphur in vaccum filter is differing with high purity.

Improving of Stret-Ford process takes place with addition of sodium - vanadiate Na₂ Vo₃ as absorption solution. It is increaseng for absorpition ability and increasing of velocity of clearing [25].

Glycol- amine method is widely using in industry for clearing of

natural gas of high pressure. For this purpose it is applied mixture of di or three ethylene glycol and monoethanol amine containing about 50% of water. process has two necessary advantages, first of all ethanol amine very effective absorbent of H_2S , Second Solubility of H_2S in this mixture is very big.

The process takes place in containing acid components not more than 20% [26] . for clearing of cokes gases from hydrogen sulphide containing acid, it has been developed new method in U.S.S.R. this method based on vacuum carbonate method [27]. It has been also developed potassium carbonate method [14] .

In this process it is usually applied as one stage of clearing gas containing of high concentration of hydrogen sulphide with next additional of mono ethanol amine solution. Absorption is taking place. in $90^\circ C$ but regeneration carried out in $105^\circ C$ and 60 atmospheres.

In western countries for clearing of cokes gases containing H_2S 50 gr/m³ it is widely used ammonia method [29].

Absorption ability of such solution is 6-7 gr of pollutants, the process is carried out in usual temperature but this method has low

degree of gas clearing from hydrogen sulphide.

2.3 - Catalytic method of neutralization of hydrogen sulphide

catalytic process are using for clearing gases from hydrogen-sulphide and different sulphur organic compounds (Thiophen, mercapitan, organic sulphide and others). As catalysts metals and its salts are using on the surfaces of carriers.

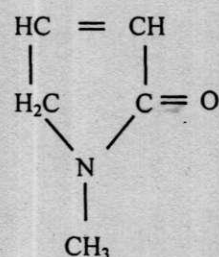
catalyst can be not only active to relation of mixtures, but can be stabled to relation of poisonous compounds. Main Processes takes plae in catalytical purification is oxidation of hydrogen sulphide H_2S till element sulphur and compounds of sulphur with other degree of oxidation.

Catalytical metod are allowing to clear till 99-99.9% these methods can be applied succesfully in high concentration of hydrogen sulphide H_2S Components in clearing gases. And this method used as additiional methods after aplication "Clous method. The best catalyst of the process of hydrogenation is compounds on the base iron, cobalt, nickel Molibden, Copper, Zinc [30]. In the oxidation proccoss more effetive are catalysts on the basis silver and gold. In clearing of natural

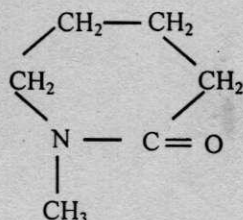
gas widely are using cobalt - molibden and nickel- moliben systems.

for clearing of basis hydrogen sulphide and sulphur oxide it is known also catalysts on the basis organic compounds:

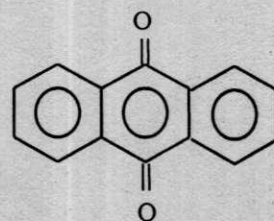
N- methyl pyrrolidon



N - methyl kaprolactam



7 - amino- 3 , 5 three azo adamantan



α - antroquione

2-4 - Electrochemical method of hydnozen sulphide H_2S

Neutralization

In oil production layer of waters containing H_2S , Hydrogen sulphide is dangerous and in presence of this compound corrsion of metal construction takes place.

In 1996, in U.SSR it was carried out experiments on

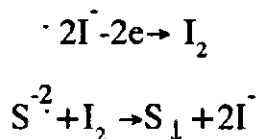
electrochemical treatment of waste waters [30]. In industrial scale method of electrochemical clearing was carried out mor late because of absence of stable material for electrods and high cost of electro energy.

Interest for using of electro chemical clearing methods appeared in soviet union and western countries [31]. First in japanse it has been prepared patent about method of waste waters treatment containing sulphur compounds. In process of electrolysis takes place solving of metal on anode. As result of this process it is formed iron sulphide which precipitate together with iron oxide - hydrate. Main advantage of electro chemical method is possibility of deep clearing from hydrogen sulphide in it concentration of wide diapazone [32-33] ^{*}.

Electrochemical method allowed neutralized all hydrogen-sulphide containing in gases and liquid in wide diapazone.

In using of this method it can be carried out automatization of technological process and use technology without of personals. we have developed electrochemical oxidation of hydrogen sulphide H_2s with help of elemental iodine and it oxygen containing compounds

prepared electrochemical oxidation- Electrochemical oxidation of iodine in solution takes place on the equation:



Summary

It has been shown that there are very effective method of purification waste industrial gases from sulphur oxide and hydrogen sulphide. But all methods have some unefficiency contented with using of many chemical compounds and much energy. Some cases this method can not be used for purification hydrogen sulphide H_2S and sulphur oxide SO_2 containing in waste in that wide diapazone.

It is Necessary to note many of this method not economically effective. that is why we try to suggest new electrochemical method based on conjugation oxidation reaction hydrogen sulphide with iodine complex and reduction iodine ion electrochemically.

CHAPTER 3 . ELECTROCHEMICAL NEUTRALIZATION OF H_2S AND SO_2 (IV) IN PRESENCE OF POTASSIUM IODINE COMPLEX

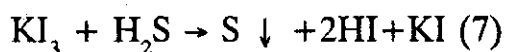
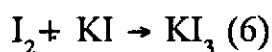
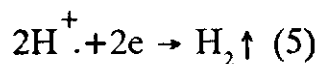
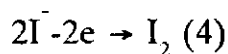
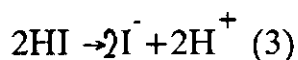
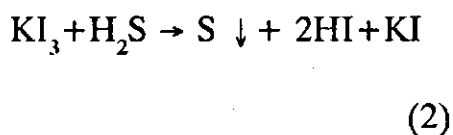
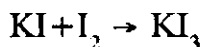
Early we showed that many scientist have investigated electrochemical neutralization hydrogen sulphide in presence of salts KI and NaI. Suggested salts are very effective reagents in electrochemical oxidation of hydrogen sulphide [31 , 32 , 33]. But in this electrochemical process separated iodine gathered on the water. In mixing Process lost of molecular iodine takas place, because of it volatility. It make this process uneffective and economically is not acceptable because of high cost of iodine molecular. It is unefficiency of this mehod. To prevent unefficiency of these methods, we suggested improved electrochemical method conncted with decreasing of volatility of molcular iodine.

For these purpose we suggest to add to solution of iodine salt . molecular iodine, which gives corresponding complex of KI_3 .

The last component is decreasing of volatility of molecular iodine and contemporary increasing economical efficiency.

The electrochemical oxidation of hydrogen sulphide in presence of potassium iodine complex takes place on next scheme.

Scheme 3.1



and do

As it is seen from scheme potassium iodine is bonded free molecular iodine giving potassium iodine complex (equation 1).

Thanks to first stage the volatility of iodine molecular don't takes place.

In second stage (equation 2) potassium iodine complex oxidized hydrogen sulphide molecule giving colloidal sulphure and hydrogen iodide HI and kalium iodide KI.

In third stage dissociation takes place rapidly (equation 3).

In fourth stage the iodine ion is oxidized in anode giving free iodine molecular (equation 4).

In fifth stage hydrogen ion electrochemically is transferring to hydrogen molecule. The free molecule of iodine formed as result of electrochemical oxidation react with KI giving KI_3 again. So the process of electrochemical oxidation iodine ion and chemical reduction free iodine molecular with hydrogen sulphide takes place conjugatively.

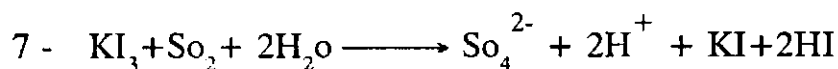
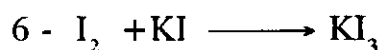
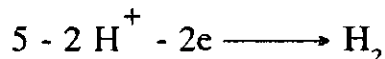
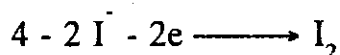
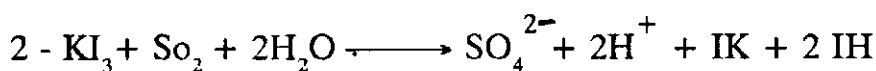
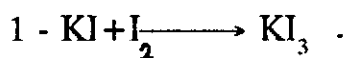
Suggested method is tested in laboratory plant and confirmed our production.

We have investigated the influence of different factors to conjugative oxidation of hydrogen sulphide in presenee of KI_3 .

We have shown that the degree of neutralization hydrogen-sulphide depends on from next factors: 1 The concentration of iodine complex, 2 - the electrical density in anode 3 - the velocity of intered gases to electrolyse gases containing hydrogen sulphide, 4 - Square of anode.

The process takes place on next chemical and electrochemical schemes:

Schem 3.2

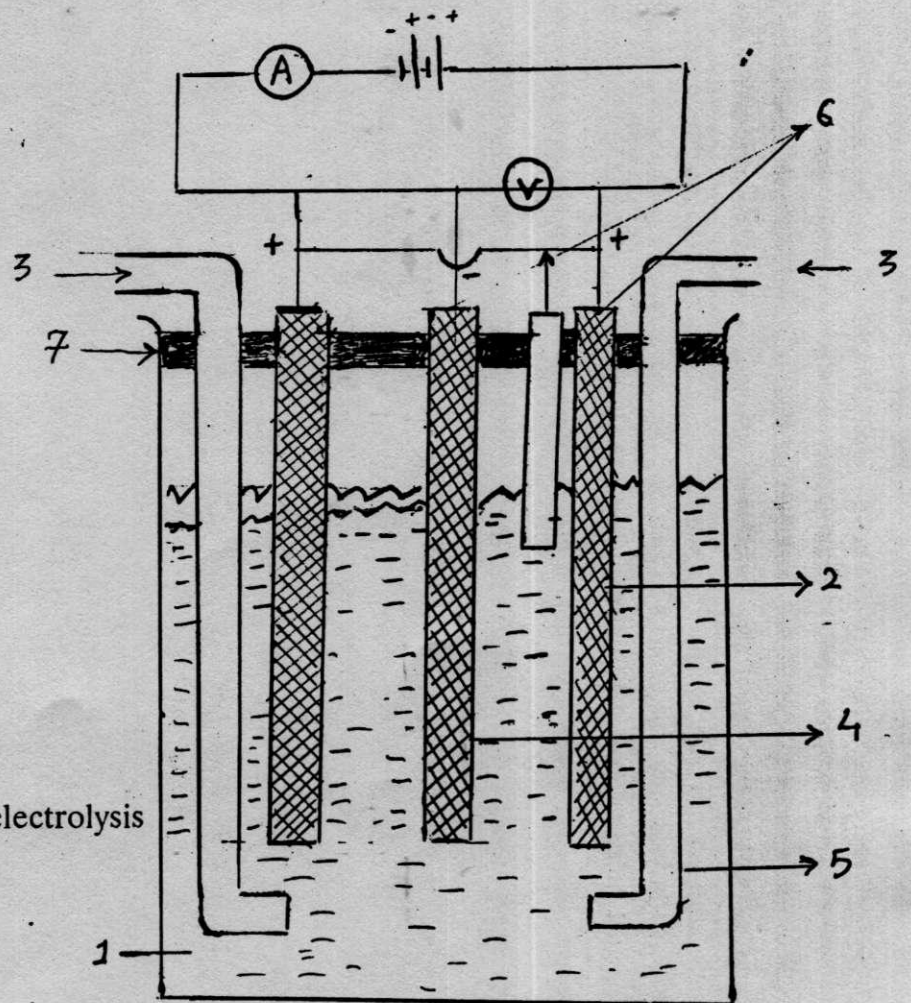


and so

As it is seen from schemes the conversion of SO_2 to SO_4^{2-} takes place by the conjugation of electrochemical oxidation of iodine ion and chemical oxidation of hydrogen SO_2 . The factors influences in conjugation oxidation of hydrogen sulphide has shown in scheme. 3.1 also is acting in conjugative oxidation sulphur dioxide (IV), Scheme-3.2.

3.1 - Investigation of many factors to degree of neutralization of hydrogen sulphide.

The main factors influence on electrochemical oxidation of hydrogen sulphide is the electrical density in anode surface.



Picture 3.1 the scheme of electrolysis

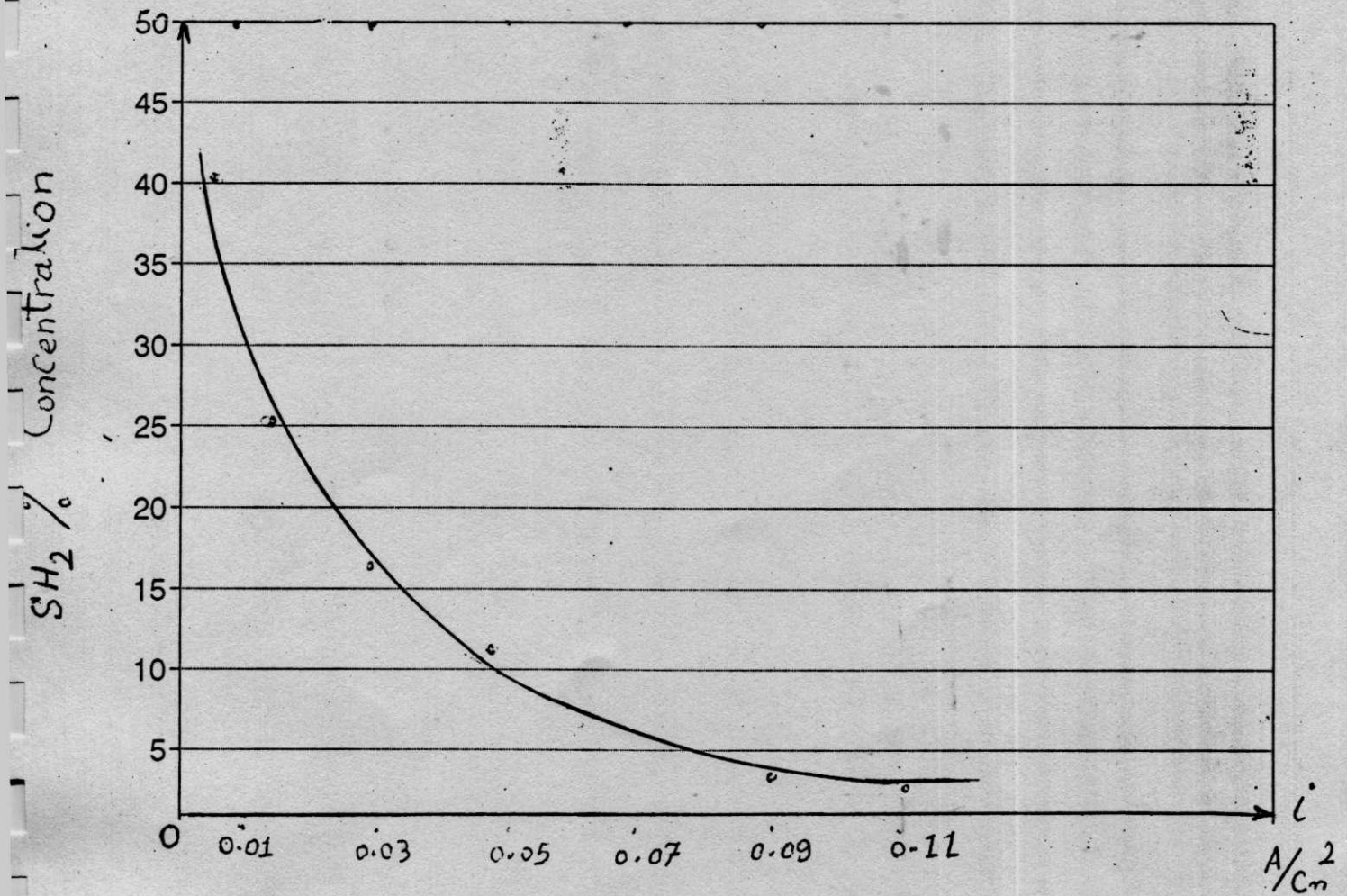
- 1 - solution of electrolyte
- 2 - Electrodes /Anode/
- 3 - Purified gas
- 4 - Cathode
- 5 - Gas distribution
- 6 - Exit of purified gas
- 7 - cap

$$i = \frac{I}{S}$$

Where i is electrical density in electrode surface.

I - is electrical intensity

S - is anode surface square.



Picture 3.2 - The dependence between i and neutralization degree of hydrogen sulphide

$[KI_3] = 0.1$ mol/lit

For investigation we have prepared a mixture gases containing 60 mg methan and 40 mg hydrogen sulphide, In electrolysis process it has been used direct electric current.

The surface of graphite anode is 40 cm^2 . The corresponding density of current is reached to change intensity of current in the anode surface.

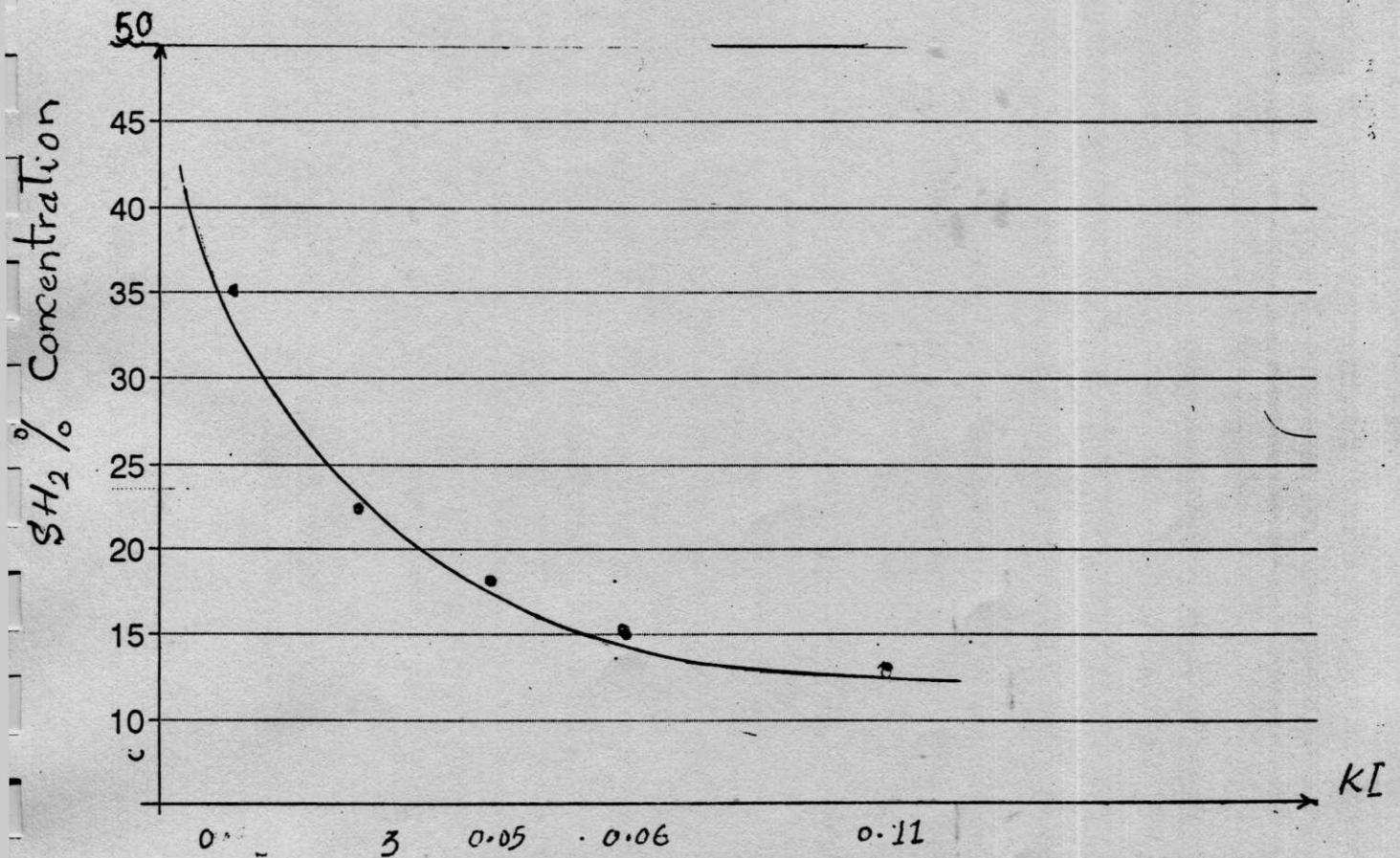
As it has been seen from picture 3.2 in increasing of electrial density the conversion of hydrogen sulphide is increasing.

The optimal density is 0.11 in which The conversion of hydrogen sulphide completly takes place. we also used the influence of temperature on the neutratization degree of hydrogen sulphide. It has been shown that temperature practically don't influence on neutralization degree in interval temperature $5-70^\circ\text{c}$. The neutratlization degree of hydrogen sulphide also depend on concentration of KI_3 . It has been shown that in increasing of concentration KI_3 the neutralization is increasing.

This result is giving in picture 3.3.

As it is seen from picture 3.3 the optimal concentration of KI_3

complex is 0.1 mol/ lit.



Picture 3.3 Dependence of neutralization degree of hydrogen-

sulphide from concentration KI₃

Optimal electrical density is 0.11 A/cm²

We also have studied the influence of velocity of intered gas to electrolyzator on neutralization degree of hydrogen sulphide.

It has been shown in little velocity of intered gas the neutrolization degree hydrogen sulphide is very high (100%).

But in increasing of velocity of neutralization gas the degree of H_2s conversion is decreasing. THE results has been shown in picture 3.4.

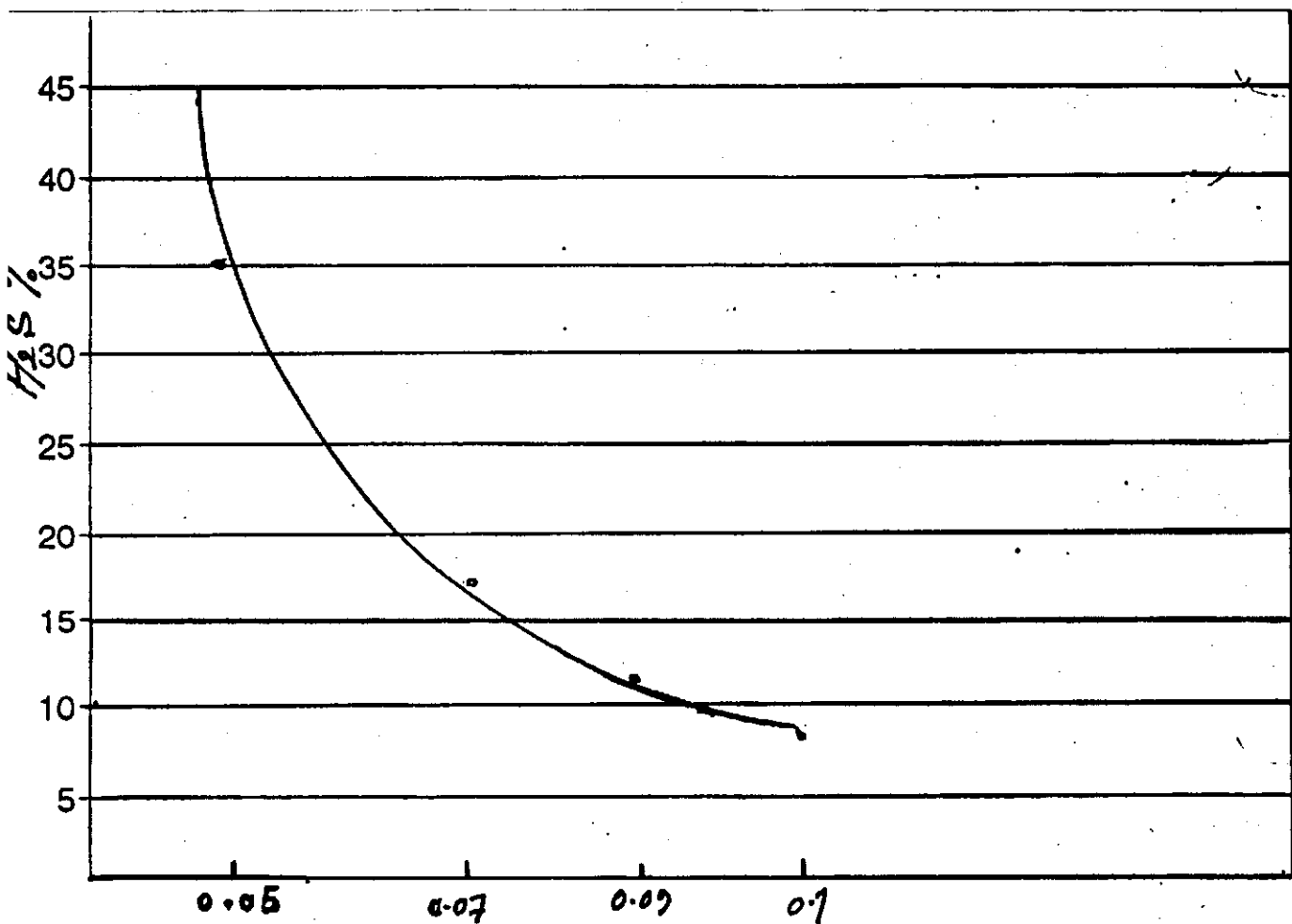
As it is seen from picture 3.4 the optimal velocity of interned gas to electrolysis is 0.11 lit/min.

We also have studied the influence of voltage to result of separation iodine in preocess of electrolysis. for this purpose we have prepared the solution of KI_3 complex in concentration 0.1 mol/lit and have placed in electrolysis chamber.

In changing of voltage of electrode from 0.05 litt 0.9 volt, the separation iodine is increasing. It has been seen from picture 3.5 that the optimal voltage for iodine separation is 0.5 volt.

The optimal voltage for iodine separation is 0.5 volt.

the mechanism of conjugated oxidation of hydrogen sulphide in



Picture 3.4 Dependence of hydrogen sulphide

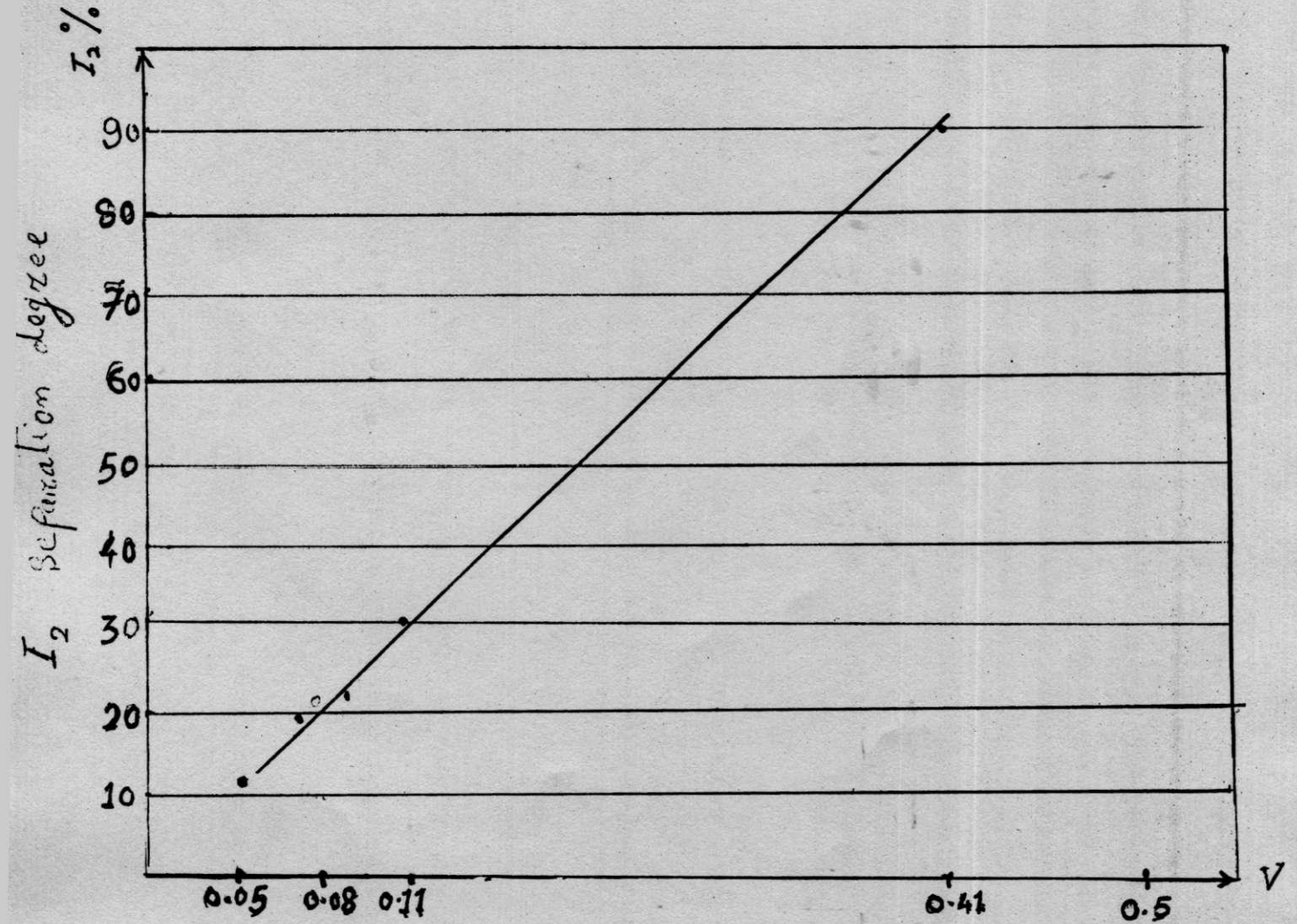
Conversion degree from velocity of interred

gas to electrolysis, Electrical density 0.11

A/cm², Concentration of KL₃ Complex 0.1

mol/lit, Voltage 0.5 V

presence KI_3 complex in electrolysis condition is very complex.



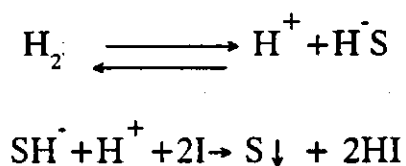
Picture 3.5 Dependence of iodine separation degree

from voltage of electrodes.

• concentration KI is 0.1 mol/lit

Electrical density is 0.11 A/cm²

Early It has been believed [35] that the oxidation takes place on the surface of electrode. Before electrochemical - conjugated oxidation the adsorption of hydrogen sulphide and iodine as an ione on the surface of electrode takes place. In the result of electrochemical oxidation of iodine anion on the surface of electrode gives iodine radical, which oxidized hydrogen sulphide. It is necessary to note the activeity of iodine radical in very high than the molecular iodine. That is why the velocity of electrochemical oxidation of hydrogen sulphide is very high and selective.



There is other opinion on the mechanism of electrochemical oxidation of hydrogen sulphide in presenec of KI_3 complex.

Many scientist believed that on the surface of electrode , iodine anion transfer to I_0^- and I_2^- and I_3^- ions. The lost ions undergoes oxidation of hydrogen sulphide in volume of solution. we believe that this opinion is not confirmed.

As result of investigation we didn't observe the formation of

other oxygen containing product of sulphur. So we have studied the electrochemical and chemical sulphur conjugative conversion reaction hydrogen sulphide in presence of KI_3 complex.

It has been shown that in the process of electrolysis the loss of iodine molecular doesn't take place, It makes this process economically useful.

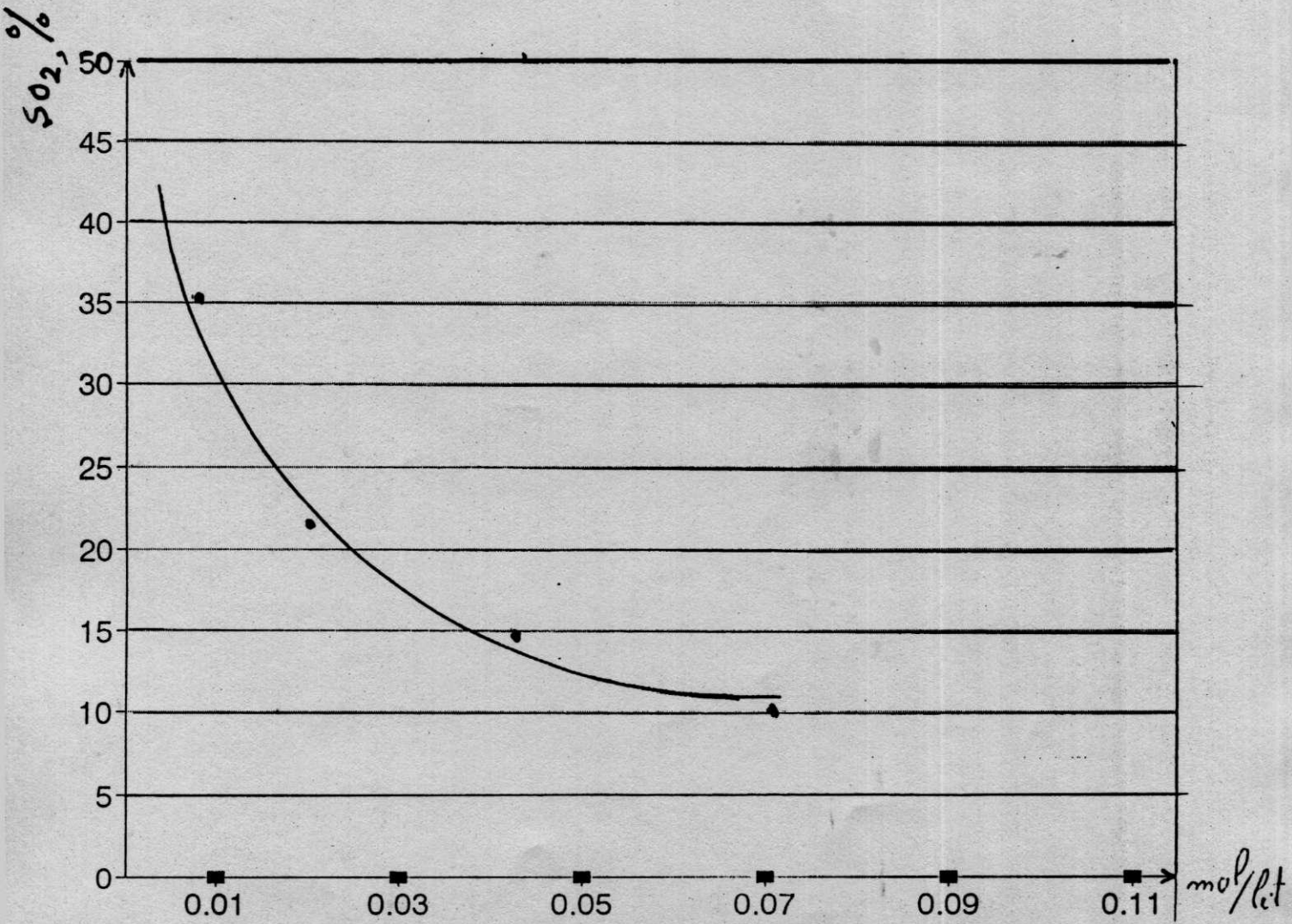
We also showed that the conjugative chemical and electrochemical oxidation hydrogen sulphide demand very little electricity energy. For neutralization 1 kg hydrogen sulphide in hydrocarbon containing gases is spending 8-10 kw electric energy. the developed method have been tested in industrial condition. for this purpose we used cracking gas containing 0.5-1% hydrogen sulphide. we have shown that completely neutralization of hydrogen sulphide takes place in optimal parameters of conjugative oxidation by our experimental studies.

My results also confirmed in laboratory of research Institute of Azarbaijan state oil academi.

3.2 - Cojugative oxidation sulphur oxide for in presence KI_3 complex.

The electrochemical, chemical conjugate oxidation of sulphur-oxide carried out in the electrolysis shown in paragraph 3.1.

We have studied the optimization of transferring conditions. the main optimization parameters are next: 1 - The concentration of iodine complex 2 - The electrical density in anode 3 - The velocity of intered gses to electrolyzer containing hydrogen - sulphide, 4 - square of anode. It has been shown that the conversion degree of sulphur dioxide depened on from concentration of KI_3 complex. the experimental result have been shown in picture 3.6

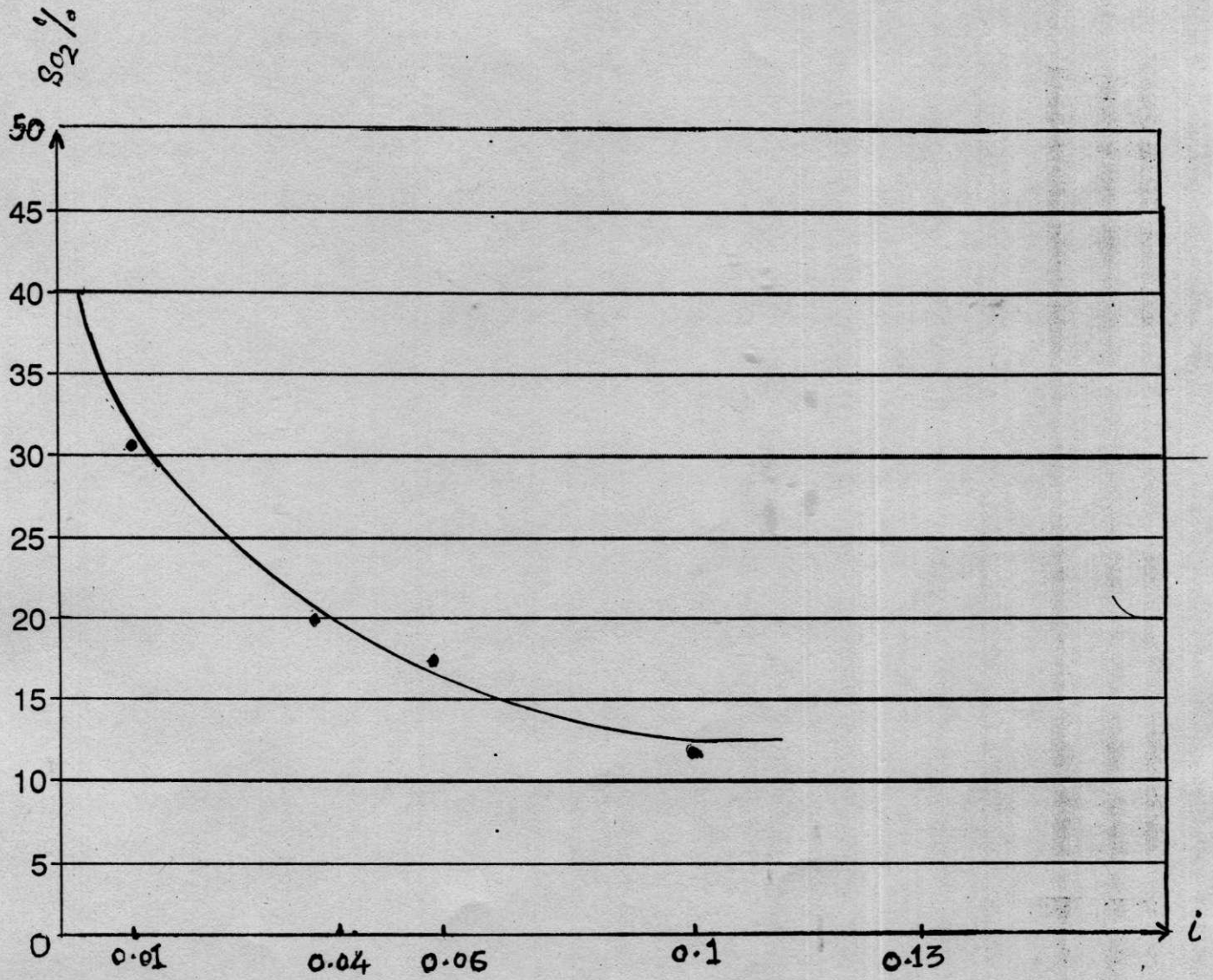


Picture 3.6 Dependence between neutralization degree of sulphur dioxide and KI₃ Concentration.
optimal electrical density is 0.11 A/cm²

As it is seen from this picture the optimal concentration of KI_3 complex, necessiated for completely neutralization of sulphur dioxide SO_2 is 0.1 mol/lit. Besides after the KI_3 concentration 0.1 the changes of conversion degree of sulphur dioxide are not observed.

The electrical density also influence of sulphur dioxide conversion degree. The experimental datas are given in picture 3.1.

As seen from this picture the optimal oxidation of sulphur-dioxide takes place in the density of $0.1 A/Cm^2$. So all electroehomical oxidation reaction takes place in low various electical fields. It means that chemical oxidation stage is more exothermic than the chemical stage. In summary entrophy of conjucative reaction has mines values.

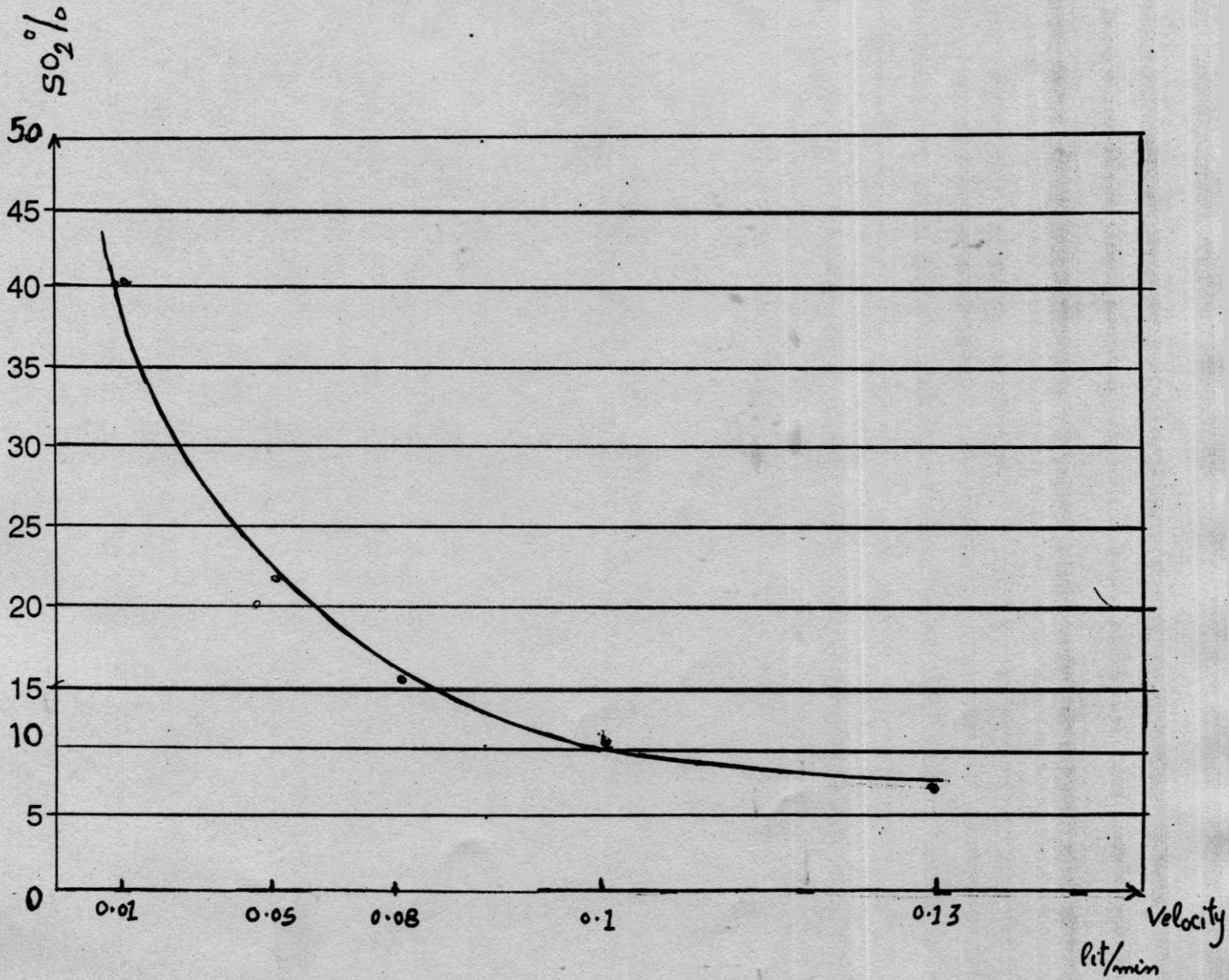


Picture 3.7 the dependence between i and neutralization degree of sulphur dioxide $[\text{KI}_3] = 0.1 \text{ mol/lit}$

We also have shown the influence of velocity of intered gas to electrolysis.

It has been stabilished that conversion of So_2 takes place completly in low various of velocity. If increase the velocity value the conversion degree of sulphrur dioxide will decrease.

All experimental datas connected with velocity of intered gase have been given in picture 3.8



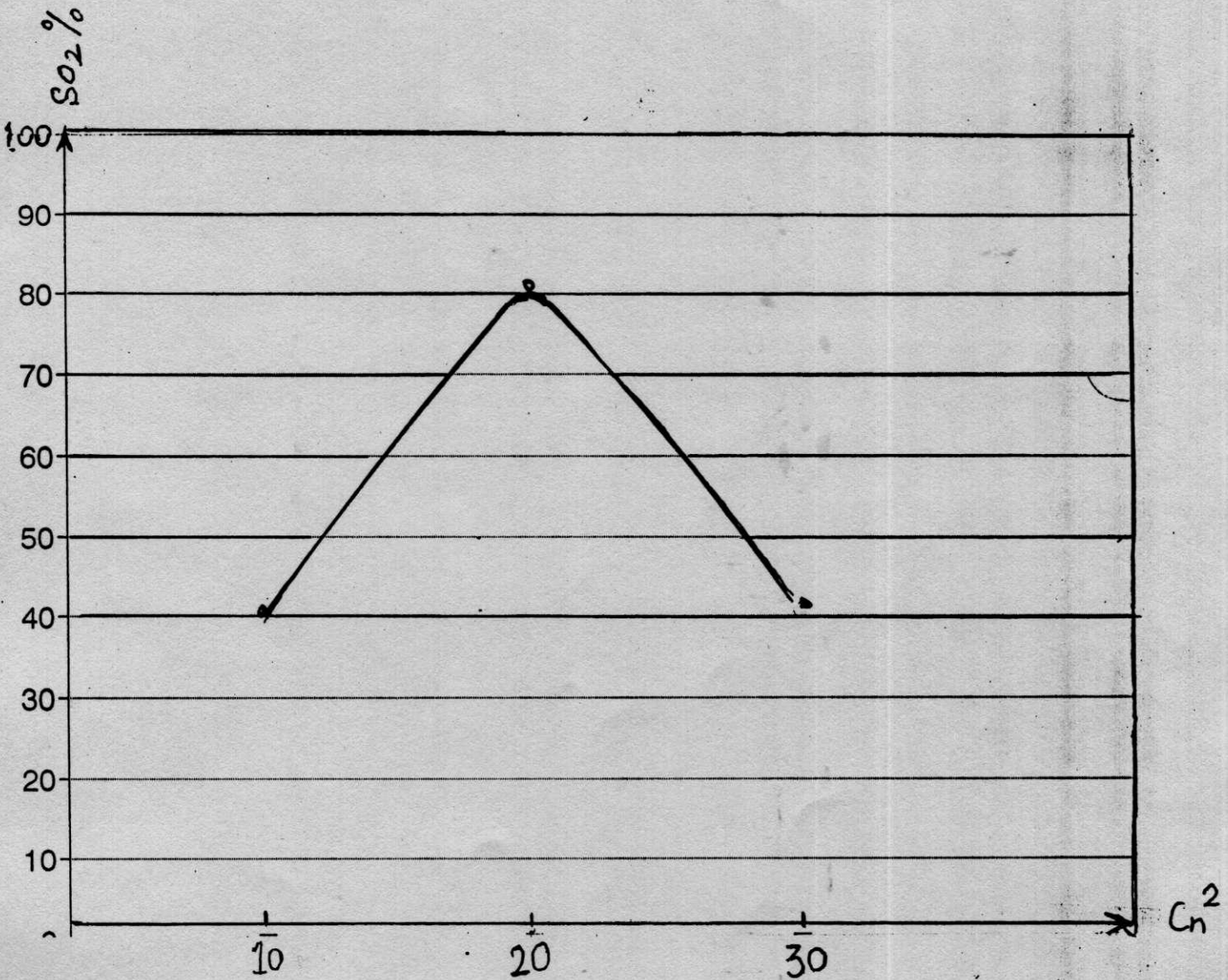
Pictur 3.8 Dependence of sulphur dioxide conversion degree from velocity of intererred gas to electrolysis. concentration of KI_3 complex is 0.1 mol/lit electrical density 0.11 A/ Cm_2 voltage 0.5v

We also established optimal value of electrode surface influence on the conversion degree sulphur oxide. In technological process this has very big meaning. The mechanism of conjugated oxidation sulphur dioxide in presence of KI_3 complex is very interesting.

In increasing of electrode surface the conversion SO_2 to SO_4^{2-} is increasing some time in constant value of electrical density equal $0.1 A/cm^2$. But after followed increasing of electrode surface the conversion degree of SO_2 is decreasing. All experimental data has been given in picture 3.9.

It has been shown the optimal electrode surface value is about $17.5 cm^2$. If electrode surface is more $7.5 cm^2$ the conversion degree of sulphur oxide is decreasing.

It means that in high electric fields takes place micro reactions connected with conversion SO_4^{2-} . It has been shown in very relatively big electric field SO_4^{2-} anion transfer to $S_2O_8^{2-}$ peroxide compound which oxidize electrode material made from graphite. In such conditions the destruction of electrode takes place intensively. It is very necessary to note it in construction of electrodes.



Picture 3.9 Dependence of sulphur dioxide conversion degree from electrode surface value, concentration of KI₃ Complex is 0.1 mol/lit
Electrical density 0.11 A/cm²
Voltage 0.5 v
Velocity of internal gas 0.1 lit / min

It has been shown the optimal electrode surface value is about 17.5 cm^2 . If electrode surface is more than 17.5 cm^2 the conversion degree of sulphur oxide will decrease. It means that in high electric fields takes place minor reactions connected with conversion SO_4^{2-} . It has been shown in very relatively big electric fields SO_4^{2-} anion transfers to $\text{S}_2\text{O}_8^{2-}$ peroxide compound which oxidize electrode material made from graphite. In such conditions the destruction of electrode takes place intensively. It is very necessary to note it in construction of electrodes.

Choosing of electrode materials also has great technological meaning.

In our process we used different electrode material made from iron, graphite, platinum and mercury. Graphite electrode is very cheap and very stable in acid and alkali conditions. But this electrodes undergoes destruction in electric field. In optimal value of electric density the destruction is minimized, for comparing of graphite electrodes with iron electrodes.

We can see that in first stage of electrolysis process conversion

takes place very increasingly. the second stage of process, the conversion of oxidize product decreasing sharply. It means that in second stage the electrochemical solving iron electrode takes place in anode intensively. we also used iron electrodes surface of which is covered with chromine metal. such kind of electrodes are stable chemically but its are unstable mechanically. very little destruction of electrode surface brings to intensive corrosion that make such electrodes economically unacceptable.

Electrode make from mercurium also are unacceptable because of it environmental points.

Platinum electrode also good and very acceptable in electrolysis process, but such electrodes very high cost. As rule this metal is not used in big plants.

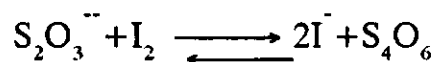
In summary we suggest graphite electrode acceptable in low electrical density. We confirm our point of view experimentaly.

3.3 - Analytical control of conjugative oxidation proecess

For investigation of conjugative chemical and electrochemical oxidation hydrogen sulphide and sulphur dioxide we used iodometrical

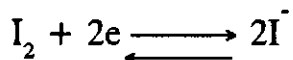
method of determination of hydrogen sulphide and sulphur oxide before and after process of conversion. For these purposes we have prepared standard solutions of chemical pure iodine. for titration of iodine excess we used standard solutions $\text{Na}_2\text{S}_2\text{O}_3$.

The concentration of standard iodine and $\text{Na}_2\text{S}_2\text{O}_3$ sodium thiosulphate were taken 0.05 mol/lit. Besides for determinations of hydrogen sulphide and sulphur oxide we used the method of gas chromatography.



Free iodine like other halogens can take electrons from substances which yield them readily (reducing agent), and is there and oxidant.

Under the influence of substances which are capable of gaining electrons (i.e oxidants) I^- ions readily give up electrons and therefore act as reducing agents. the iodometric method of volumetric analysis is based on oxidation- reduction processes involving interconversion of elemental and I^- ions:

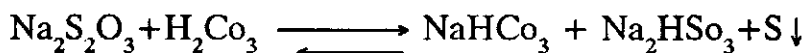


The standard oxidation potential of $I_2/2I^-$ system has the relatively low value of 0.54 v. It follows that, in contrast that, in contrast to the oxidizing agents already considered K_2MnO_4 and $K_2Cr_2O_7$, I_2 is a relatively weak oxidant.

3.3.1 -Preparation of standard solution of $Na_2S_2O_3$

The high sensitivity of the iodine- starch solution ensures a quite distinct blue colour in 50 ml of solution with one drop of 0.01N iodine solution. Accordingly, it is possible to use 0.02N rather than 0.1 N standard iodine and thiosulphate solutions. It is known that the drop error in titration diminishes with decreasing concentration of standard solutions. Moreover, in this case the saving of such relatively costly reagents as KI and I_2 is also important.

Sodium thiosulphate, $Na_2S_2O_3 \cdot 5H_2O$, is a crystalline substance. Although it can be obtained chemically pure under the appropriate conditions, standard thiosulphate doesn't conform to the requirements for primary standards. It is a relatively unstable compound; for example, it reacts with carbonic acid dissolved in water as follows:



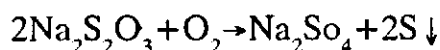
As a result, the normality of thiosulphate solution increases somewhat. the gram - equivalent of $\text{Na}_2\text{S}_2\text{O}_3$ is 1 M . whereas that of NaHSO_3 is $\frac{1}{2}$ M. Therefore , in the above reaction one gram - equivalent of $\text{Na}_2\text{S}_2\text{O}_3$ yields two gram - equivalent of NaHSO_3 .

The following is evident from this.

- a) It is pointless to weigh $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ out exactly.
- b) The solution must not be standardized at once, but about 10 days after preparation. However, if freshly boiled and cooled distilled water is used and 0.1 gr of Na_2CO_3 Per litre of solution is added to stabilize the litre.

The solution may be standardized on the day after preparation The $\text{Na}_2\text{S}_2\text{O}_3$ Solution must be kept in bottles protected from CO_2 by a tube containing soda lime on ascarite , in the same way as NaOH solutions. Subsequently the titre of $\text{Na}_2\text{S}_2\text{O}_3$ gradually decrease, so that it must be checked from time to time. the decrease of the titre is due to following causes:

- 1) oxidation of $\text{Na}_2\text{S}_2\text{O}_3$ by atmospheric oxygen:



2) Decomposition of $\text{Na}_2\text{S}_2\text{O}_3$ by the action of microorganisms (thio bacteria); this is main cause of the instability of thiosulphate solutions. To prevent this decomposition, 10 mg of mercuric iodine HgI_2 per litre of solutions may be added as an antiseptic, the solution should also be effectively protected from light, which favours the growth of these bacteria.

Base your preparation of thiosulphate solution on the value of its gram- equivalent and required normality (about 0.02), and take into account all the points discussed above.

Iodine solution: standard iodine solution may be prepared either by exact weighing of chemically pure crystalline iodine, or from commercial iodine. In the later case the solution is usually standardized against standard thiosulphate solution. let us consider both these methods.

Preparation of iodine solution by weighing chemically pure iodine. Commercial iodine contains chlorine, various compounds of iodine. with other, such as ICl , IBr , ICl_3 and hygroscopic moisture. the principle on which its purification is based is that the vapour pressure at a temperature below its melting point. therefore, when solid

iodine is heated it passes into vapour state without melting, and the vapour condenses in the form of crystals on formation of a liquid phase is known as sublimation. the impurities in it must be converted into non- volatile substances- for this commercial iodine is ground in a mortar with KI and Cao.

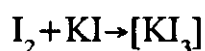
calcium oxide absorbs water and forms $\text{Ca}(\text{OH})_2$, while KI reacts with iodine halides to form free iodine and non- volatile salts, eg:



A mixture of commercial iodine with KI and Cao is put in a perfectly dry beaker which is covered by a round - bottomed flask filled with cold water, and is warmed cautiously on a hot plate. from time to time the iodine crystals deposited on the cold flask are transferred by means of a glass rod to a previously weighed watch glass. which is weighed on a technical balance. the sublimation is countinued until enough sublimed iodine has been obtained for preparation of the solution . In this Case 250 ml of 0.02 N iodine solution is sufficient. since the gram- equivalent of iodine is equal to the gram - atom, 126.9 gr, the amount required is $\frac{126.9 \times 0.02 \times 250}{1000} \approx 0.06 \text{ gr I}_2$, when preparing the iodine

solution, remember that iodine is volatile and that its vapour poisons the laboratory air and corrodes the metal parts of instruments. Therefore, all operations involving the handling and sublimation of iodine, etc; must be performed in the fume cupboard.

The analytical balance, especially, must be protected against the action of iodine vapour. As already stated, the solubility of iodine in water is very low; it is there for dissolved in concentrated solutions of KI, with which it forms a soluble red- brown complex compound.



At least three times as much KI as iodine by weight should be taken to ensure easy and quick dissolution- Moreover, the volatility of iodine must be taken into account when it is weighed. It is best to weigh iodine in dissolved form, as iodine solutions in KI are less volatile. To do this, proceed as follows. first weigh out on the technical balance about 2-3 gr of crystalline KI in a weighing bottle and dissolve it in the minimum quantity of water. when the solution has reached the temperature of surroundings (heat is absorbed when KI dissolves) Cover the weighing bottle with its lid and weigh it accurately on the analytical balance. Now transfer the required amount bottle with

potassium iodide solution (this operation is performed in the fume cupboard), Cover at once with the lid, and weigh the bottle accurately again. the difference between the two weighings gives the weigh of iodine taken. cautiously agitate the solution in stoppered weighing bottle until the iodine cryrtals dissolve.

Completly and then pour the solutions through a funnel into a 250 ml measuring flask. carefully into this flask, make the solution up to the mark with water, close the flask with a glass stopper, and mix the solution throughly.

3.3.2 Standandization of $\text{Na}_2\text{S}_2\text{O}_3$ solution

Numerous primary standards have been proposed for standartization of $\text{Na}_2\text{S}_2\text{O}_3$; they include solid chemically pure iodine, potassium- iodate KIO_3 , potassium bromate KBrO_3 , potassium fericyanide $\text{K}_3[\text{Fe}(\text{CN})_5]$, potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$, etc. It is possible also to standardize $\text{Na}_2\text{S}_2\text{O}_3$ with the acid of standard KMnO_4 Solution. This method is interesting because it links the iodometric and permanganate methods. However, it is less accurate. Potassium bichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, is most often used in practice. Pure

potassium bichromate can be obtained by the recrystallization from water and drying at 200°C. The solution is greatly diluted with water before titration. Therefore standardization of $\text{Na}_2\text{S}_2\text{O}_3$ is based on the general principles of iodometric determination of oxidizing agent. First, and exactly measured volume of standard potassium bichromate $\text{K}_2\text{Cr}_2\text{O}_7$ solution is added to a mixture of KI and H_2SO_4 . The $\text{K}_2\text{Cr}_2\text{O}_7$ is then replaced by an equivalent amount of free elemental iodine, which is titrated with thiosulphate solution to be standardized. preparation of standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution.

Since the $\text{K}_2\text{Cr}_2\text{O}_7$ molecule gains six electrons in the reaction with KI, the gram-equivalent of $\text{K}_2\text{Cr}_2\text{O}_7$ is:

$$\text{g-eq of } \text{K}_2\text{Cr}_2\text{O}_7 = \frac{M}{6} = 49.30 \text{ g}$$

For preparation of 250 ml of approximately 0.02 N Solution it is evaluated the amount of $\text{K}_2\text{Cr}_2\text{O}_7$, mass of $\text{K}_2\text{Cr}_2\text{O}_7$ accurately in analytical balance by the usual method, transfer it quantitatively 250 ml measuring flask, make it up to the mark with water and mix. Calculate the normality of the solution.

Titration carried out as general acceptable method. For

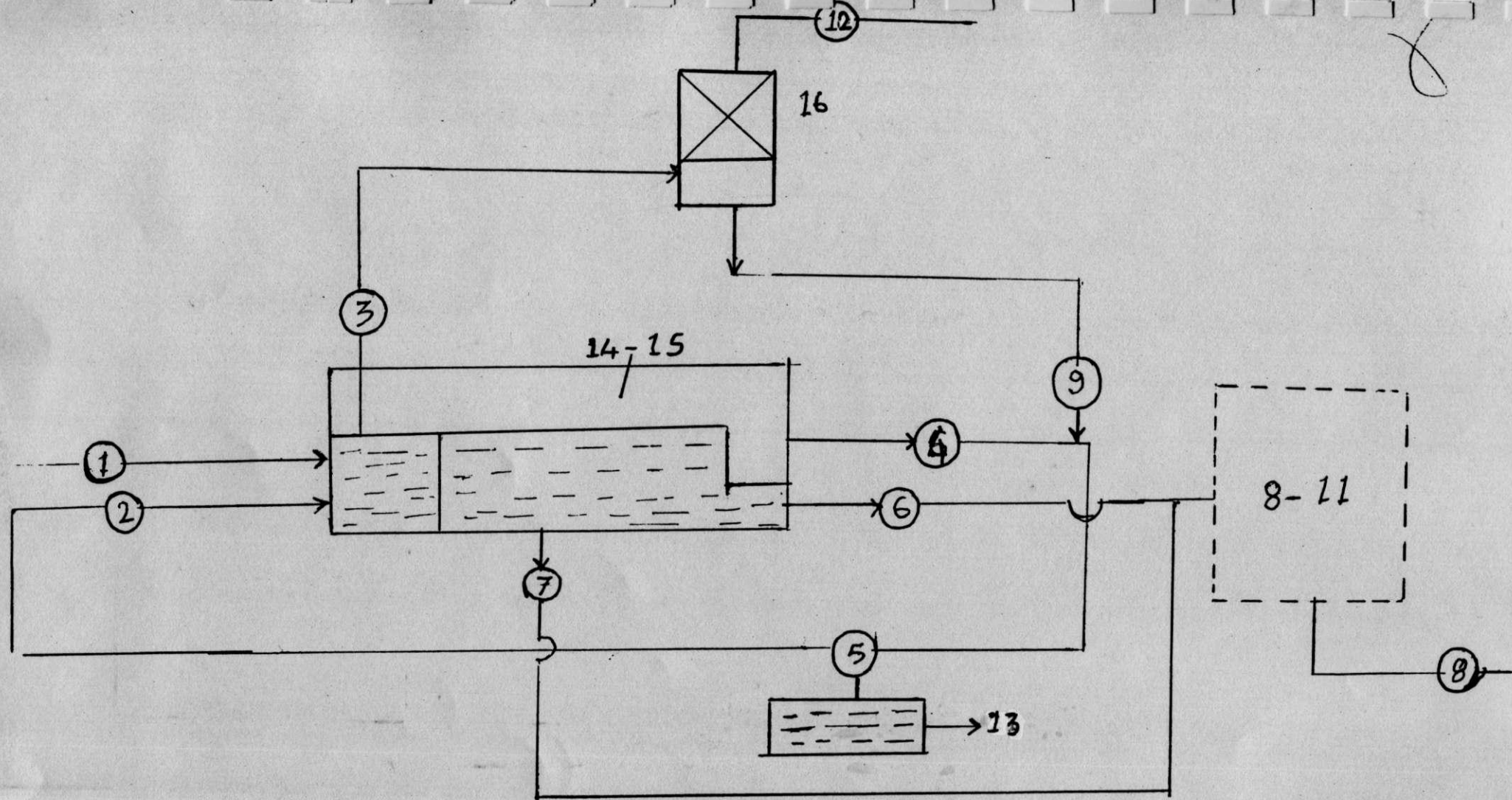
calculation we used general acceptable equation.

$$N_1 V_1 = N_2 V_2$$

3.4 . Principal technological scheme of neutraliation ^{of} waste gases containing hydrogen sulphide and sulphur dioxide.

On the basis of experimental datas given in chapter 2 and 3 we suggest new technology scheme of plant able to clear about 1500-1520 M³ in hours wast gases. the scheme of his plant is given in picture 3.10.

This plant which we described in picture 3.10 it can be purified cracking and other waste gases containing hydrogen sulphide and sulphur dioxide. clearing ^{of} hydrocarbon gas with known contents from plant of caltalytic cracking (1), is directed to electrolysis section of electro floater (2), where, it chemical oxidation takes place. clearing gas with containing hydrogen sulphide and sulphur oxide .



Picture 3.10 - Block- scheme of material flow of plant on purification hydrocarbon gases from hydrogen sulphide and sulphur oxide (IV)

2 - Electrolyzator, - floatator, 16 - separator, 13 - Tank for solution, 8 - 11 Blok for separation of sulphur

In fuel system. Gas entered to purification system in temperature of surrounding at pressure 1.3 - 1.5 atmospheres.

To electrolyzator from energy block via adaptor is given direct electric current which potential till 4V (working potential) and current with capacity till 100 k A/h. In electrolytical section it has been established anode- cathode electrode block. separated in oxidation process dispersion - colloidal sulphur is floated with help of bubble and separated in process of electrolysis gas via hydro by its flowing direct to tank of scum, from where it is directed to pressure tank (8) , where it is melted with help of sharp water steam in temperature 150 °C in period of one hour.

Then after some time melted sulphur is pressed to tank (9), where additionally it is stayed, is lead to phase, low layers of sulphur (10) is pouring from (10) and it is sending to market.

Steam condensed with formed sludge periodically is pouring to canalization.

Temperature in clearing system mainly depend on from temperature of intered to purified gas in interval of temperature 15-40°C.

Scum of sulphur is gathering on the Surface of electrolyte is suspension which help of scrub is gathered to collector of scum and, ther via hydro by its flowing is running and gathering into scum tank (7).

The contents of gas fraction often prufication is given in table

3.1.0

Contents of	H ₂	CH ₄	ΣC ₂	C ₃ H ₈	C ₃ H ₆	C ₄ H ₁₀	C ₄ H ₈	C ₅ H ₁₂	C ₅ H ₁₂	SH ₂	O ₂
gas percentage	1	2	3	4	5	6	7	8	9	10	11
Concentraation	1.08	15.45	35.96	8.79	7.56	5.30	3.0	1.9	2.0	0.008	0.0084

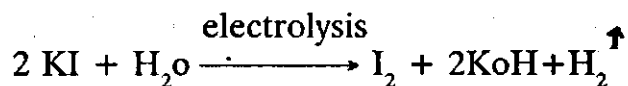
Gas fraction is formed in amount of 9500 M³/h. The medium density of gas is 1:056 gr/lit.

In addition to gas, secondary components in the plant is absent.

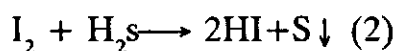
3.5 . *Material balance of clearing plant hydrocarbons from hydrogen sulphide*

On the base clearing method and evaluation of material balance have been put chemical and electrochemical process take placed in electrolytic section of main aparatus of plant:

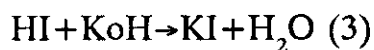
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-
- 1 - Electrochemical Reduction of KI from water solution to molecular iodine.



- 2 - chemical oxidation with separated molecular iodine of hydrogen - sulphide containing in purified hydrocarbon gas.



- 3 - chemical neutralization of formed HI by KOH



- 4 - Assumed technology is allowing to purify hydrocarbon gas not containing oxygen (not more 0.50) with concentration of H_2S till 100%.

3.5.1 - Initial data for calculation of material balance.

- 1 - The amount of clearing of hydrocarbon gas. Gas will be entered to clearing from plant of catalytic Cracking. The general volume of clearing gases is $9500 \text{ m}^3/\text{h}$, Containing 0.42 volum percentages or 1.79 M/h or 6.7 K M/h.
- 2 - In table 3.2 is given the content of hydrocarbon gases on every

plant and medium contents on gases

- 3 - concentration of potassium iodide KI in circulation solution of electrolyte 0.5%

Contents of clearing gas Table 3.2

Contents%	H ₂	CH ₄ ΣC ₂	i-C ₃ H ₆	n-C ₃ H ₆	i-C ₄ H ₁₀	n-C ₄ H ₁₀	C ₄ H ₈	iC ₅ H ₁₂	nC ₅ H ₁₂	H ₂ S
Source of gas	1	2	3	4	5	6	7	8	9	10
Plant No 55	0.6	16.5	41.4	2.5	21.3	6.5	9.2	0.80	0.80	0.2
Plant NO43	0.6	13.4	23.2	22.6	8.1	2.8	8.7	7.7	4.3	0.9
Medium Contents of gas	0.6	15.5	35.9	35.9	17.58	5.3	9.0	3.0	1.9	0.42

The density of gas in plant No43 - 1.074 g/lit

the density of gas in plant No 55- 1.043 g/lit

- 3 - Concentration of potassium iodide KI in circulation solution of electrolyte - 5%

- 4 - Assumed concentration of hydrogen sulphide in purified gas from trace till 100%

- 5 - yield of iodine on the current -95%

- 6 - As electrodes it is recommended anode and cathode from ORTA

(oxides of Ruthenium and titanium which covered to titanium - base) with thickness 2 mm

- 7 - Content of electrolyte in exit and enter to electrolyzer.
- 8 - Content of electrolysis gases separated in electrolysis KJ (ignoring - content of clearing gas)

Hydrogen - 98%

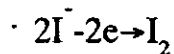
oxygen - 1.5 %

- 9 - Lost of KJ in process of circulation - 0.5%
- 10 - the degree of gas clearing from hydrogen sulphide 98.0%
- 11 - Concentration of hydrogen sulphide in exit of plant-not more 20 g/M³
- 12 - the lost of formed sulphur - 5.0 %

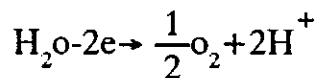
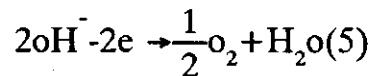
3.5.2 -Material balance of processes carried out in electro-chemical section

According to equation 2 for oxidation 1.79 KM (60.9Kg) it is necessary 1.79 KM (455.7Kg) iodine. In this cases it is formed 1.79 KM/h (61Kg/h) sulphur. Formed on equation 2, HI (3.9 KM) is reacted with the same amount of KoH, formed on equation 1 ; that

bring to completely regeneration KI (3.58 KM), or reaction takes place on the anode:



The same time on the anode process of discharging of ions OH^- of molecule of water takes place.



The relative velocities of separation on the anode of iodine and oxygen depend on condition of carrying out of electrolysis process. In our conditions carrying out of process anode ORTA, temperature 60°C . on the basis of experimental data, Concentration of oxygen in separated gas (hydrogen) is 1.56% by volume, in this cases according to stoichiometric of equation (5 and 6), 1 KM oxidated hydrogen gives 1 KM water. In this process it will be separated 1.79 Km (3.58 Kg/h)hydrogen.

3.5.3 -Explanation of table 3.3

1 - In material balance it is not given the amount and content of clearing gas ($9500\text{M}^3/\text{h}$). In addition to hydrogen sulphide,

oxidized till sulphurs.

- 2 - To system of clearing it is added twice amount of KI necessiated for bonding iodine in complex KI_3 . It is 340 M³ of water.

table 3.3

Flowing Component	1		2		3		4		5		6		7		8		9		10	
	kmol/h	kg/h	kmol/h	kg/h	kmol/h	kg/h	kmol/h	kg/h	kmol/h	kg/h	kmol/h	kg/h	kmol/h	kg/h	kmol/h	kg/h	kmol/h	kg/h	kmol/h	kg/h
H ₂ S	1.79	6.8			0.036	1.22													0.056	1.22
KI				5943				5646 5943		5646 5943		2017		2017						
S													56.73							
H ₂					1.8	3.6													1.8	3.9
H ₂ O				24000		1670		2170		21370		600		600				200		1470

Not : iodine formed in electrolysis of KI is reacted completely, therefore it is ignored in material balance (70)

Summary

It has been suggested new technology of neutralization of hydrogen sulphide containing hydrocarbon waste gases.

- 1 - It has been shown that in process of electrochemical oxidation of hydrogen sulphide in presence of potassium iodine - iodine complex KI_3 gives colloidal sulphur and conversion of hydrogen sulphide till sulphur takes place completely.
- 2 - It has been studied the influence of next factors on the conversion of hydrogen sulphide: Concentration of potassium iodate - iodine complex electric density of anode, temperature, velocity of intered to electrolysis hydrogen sulphide containing gases and surface of electrode.
- 3 - It has been shown that in increasing electric density on the anode the conversion of hydrogen sulphide till sulphur also increasing. It has been found the optimal various of oxidizing hydrogen-sulphide parametres.
- 4 - It has been investigated the conjucative oxidation of sulphur dioxide in presenee of potassium iodide - iodine complex. It has

been determined values of main factors affected to conversion degree of sulphur oxide.

- 5 - It has been suggested principal technological scheme of purification of hydrocarbon gases (cracking gases), containing hydrogen sulphide.

LITERATURE

1. Lea F.M., Nurse R.W. Symposium on particle size analysis
Inst, Chem. Engng and soc. Chem Ind., P.47 Feb, 1947
2. Katz M., Cole R.I. Ind. Engng. Chem., 42, 2298, 1950
3. Bienstock D., Brunn L.W., Murphy E.M. Beson H.E.
Shulphur dioxide, 1958
4. Fleming E.P., Fitt T.E. Ind -Engng chem 42-22-52, 1990
5. Kohl A.L., Riesen Leld F.C. Gas Purification, M.C.Graw -
Hill New York, 1960
6. Bromley L.A., Read S.M. Removal of sulphur oxide from
stack gases by sea waters.
7. Pearson T.L., Nonhebel G., Ulanden P.H. N.T Inst fiel 8,119,
1935
8. Francis W., Hepper G.H - Engineering, 172, 36, 1951
9. Atsukawa M., Mishimoto Y., Matsumoto K. - Mitsubishi
Heavy industries LTD Technical
10. Strauss W., The Control of sulphur emissions from
Combustion Processes In Air Pollution Control Ed. St.
11. Allcut A.E. - Proc Instin. Mech. Engrs. 140, 308, 1938
12. Kennaway T., Iron and steel Institute special Report, № 61,
P. 139

-
13. Wallis E. - Brit. Chem. Engng. 7, 833, 1962
 14. Wood C.W. - Trans Instn. Chem.Engrs., London 33, 54, 1960
 15. Pitelina N.P. Chemical Purification of effluent gases. Pafer VII - 119 PP. 119-23 W.H.O. Int Reinal Seminar, Moscow - Volgograd 31st Aug 20th Sept, 1967
 16. Atsukawa M., Mishimoto Y., Matsumoto K. Mitsubishi Heavy Industries LTD Technical Review, 3. 134, 1969
 17. Anon: A.Digest of state Air pollution laws, 1967 edition M.S. Dept of H.E.W., Public Healt Service. Washington D.C/20201 P. 656, 1968
 18. Shale C.C., Simpson P.G., Lewis P.S., Removal G. Sulphur and nitrogen oxide from stack gases by ammonia, A.I. Ch. E. Ann. Meeting, Washington D.C., 1969
 19. Yavorsky P.M. Mazzoco N.T. Rutledge G.D., Gorin E-Env Sci Tech 4, 757, 1970
 20. А.Л.Шабанов, Л.Годик, Механизмы окисления сероводорода на электроде. Азербайджанское Нефтяное Хозяйство. № 7, 1987, С.38-44.
 21. А.Л.Шабанов Аналитик кимјанын эсаслары 1997, С.295

34. Алексеев В.Н. «Количественный анализ» Госхимиздат,
1972

35. Л.Годик Канд. диссерт. Электрохимические и
сопряженные окисление сероводорода в природных газах.
Баку, 1987, С. 220