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54 **Method for removal of iodine in gas.**

57 A method for the removal of iodine from a mixture gas or vapor, in which iodine is removed as a sediment of an insoluble iodine compounds by bringing the mixture gas or vapor into contact with a solution containing silver ions, is disclosed.

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METHOD FOR REMOVAL OF IODINE IN GAS

Field of the Invention

The present invention relates to a method for the removal of iodine and/or iodine compounds from mixture gases.

Prior Art

Many methods have been proposed for the removal of iodine species contained in dissolver off gases (hereafter referred to as "DOG") from spent nuclear fuel reprocessing plants. These include wet methods such as the alkaline scrubbing process, Mercurex process, and Iodox process, and the dry methods which use various kinds of solid adsorbents.

In the alkaline scrubbing process, a solution of 1 - 2 mol/l caustic soda is used to absorb iodine from the DOG. The scrub liquor produced contains iodine compounds such as NaI, NaOI, and NaIO₃. The disadvantage of this method is that a great deal of sludge is produced due to reaction of caustic soda with CO₂ and nitrogen oxides (hereafter referred to as NO_x) in the DOG, in addition to the sediment of iodine compounds produced, so that the amount of radioactive waste to be treated remarkably increases as well as the expense of such disposal. (Literature: (1) Holladay, D.W., 1979, A literature survey: methods of the removal of iodine species from off-gases and liquid waste streams of nuclear power and nuclear fuel reprocessing plants, with emphasis on solid sorbents. ORNL/TM-6350; (2) International Atomic Energy Agency, 1980, Radioiodine removal in nuclear facilities; Technical reports series No. 201, IAEA, Vienna; (3) Benedict, M., T.H. Pigford and H.W. Levi, 1981, Nuclear Chemical Engineering, McGraw-Hill N.Y.).

The Mercurex process uses a nitric acid solution of mercuric nitrate (1-14 mol/l) as a scrubbing solution into which iodine compounds are absorbed and converted to HgI₂ or Hg(IO₃) to be thereafter removed. Due to the use of mercury in this process, careful countermeasures are required to eliminate mercury pollution. (Refer to the above literature (1), (2) and (3).) In the disclosed Mercurex process, the solution of mercuric nitrate loaded with iodine and mercury, and then iodine, is fixed as copper iodide and the mercury is recycled for reuse. The design of this process is thus com-

plicated. (Literature: (4) Collad, G.E. et al., 1978, Iodine trapping and conditioning in the Mercurex system, 16th DOE Nuclear Air Cleaning Conference, p 552)

The Iodox process uses a highly concentrated nitric acid of 20 - 22m mol/l as a liquid absorbent to precipitate and recover iodine compounds as HI₃O₈. The corrosion of the equipment materials of construction by the concentrated nitric acid used is a serious disadvantage of this process. (Refer to the above literature references (1), (2) and (3).)

Most of the dry methods utilizing solid adsorbents for the removal of iodine are based on the reactions of silver or a silver salt with iodine. For example, AC6120 is a sorbent consisting of amorphous silicic acid base material impregnated with silver nitrate, which is capable of efficiently absorbing and removing iodine even in the presence of NO_x. (Refer to the literature reference (5): Japanese Patent SHO. 53-22077.) It is necessary, however, to heat DOG to approximately 150°C to assure a rapid reaction of silver nitrate with iodine and iodine compounds. (Refer to the literature references (2) and (3)).

The Hanford Plant in the United States has achieved acceptable results in iodine removal using a solid adsorbent consisting of unglazed saddles impregnated with silver nitrate. Heating of the DOG is also necessary for the use of this adsorbent, however, and it has been reported that the reaction of silver and iodine will not take place at a temperature lower than 110°C. (Literature references: (3) and (6) "Nuclear Chemical Engineering" by Hiroshi Yamamoto, 1976, published by Nikkan Kogyo Shimbun).

Various types of silver-exchanged zeolites have been reported to be useful for the removal of iodine in the DOG. These adsorbents also requires an elevation of the temperature of the DOG to 100°C or higher as in the case of the above systems. (Literature references: (2) and (7) Thomas, T.R., B.A. Stapeles and L.P. Murphy, 1978, The development of AgZ for bulk ¹²⁹I storage. Proc. 15th DOE Nuclear Air Cleaning Conference, p 394).

The common disadvantage of the foregoing systems using such solid adsorbents is that, in the storage and final disposal of the spent adsorbents loaded with radioactive iodine, the extra volumes of the carriers are definitely disadvantageous in that the carriers having such surplus volume must also be treated as radioactive wastes.

Objects of the Invention

An object of the present invention is to provide a system which does not possess the disadvantages of the wet and dry processes described above, which can be simple in structure, which does not produce extra waste other than iodine compounds, which does not require preheating of the DOG, which does not use corrosive or hazardous chemicals such as nitric acid and mercury, and which is free from the effects of NO_x and water vapor present in the DOG. Other objects of the invention will become apparent hereinafter, and still others will be obvious to one skilled in the art.

Brief Description of the Drawings

FIGS. 1 to 4 are explanatory diagrams illustrating the effects of the method of the present invention.

Description of the Invention

The objects of the present invention can be achieved by contacting mixture gases or vapors containing iodine and/or iodine compounds, such as methyl iodide with a solution containing silver ion and by removing iodine species contained in the said gases or vapors as a sediment or precipitate of insoluble iodides. The present invention makes use of wet contact between mixture gases or vapors containing iodine and/or iodine compounds with a solution containing silver ion, and belongs to the category of wet processes rather than dry process in which silver salt is impregnated into or onto solid substrates.

To prepare the solution containing silver ion, various kinds of silver salts such as silver nitrate, silver sulfate, and silver carbonate, can be used. The concentration of silver ion can range between 0.0001 and 5 mol/l, preferably between 0.001 and 1 mol/l. The solutions may contain mineral acids such as nitric acid. As equipment for gas-liquid contact of the solution containing silver ion and a gas to be processed, one can use almost any type of equipment including conventional equipment such as a bubble tower, spray tower, plate column, wetted wall column, or the like, as well as newer types of gas-liquid contact equipment.

Mixture gases or vapors containing iodine and/or iodine compounds to be processed by the system in accordance with the present invention may contain, for example, about 2000 ppm of nitrogen dioxide and/or 0.5% of water vapor in addition to the iodine of any concentration, and it has been established that the presence of these substances

does not adversely affect the absorption efficiency of iodine species. The process of the present invention therefore permits direct introduction of the gas containing iodine into the gas-liquid contact equipment without pretreatment which, as well as the simplicity of the post-processing equipment, allows extremely simplified design. According to the process of the present invention, iodine which precipitates as insoluble iodide can readily be separated by any usual method. Only this sediment needs to be removed as radioactive waste according to the system of the present invention and the quantity of radioactive waste is therefore much less than when using conventional dry or wet methods, this being one of the important advantages of the present invention.

Detailed Description of the Invention

The following Examples describe in detail the system in accordance with the present invention, but are not to be construed as limiting.

Example 1.

A dry air containing 200 ppm of iodine was allowed to pass at a rate of 0.5 l/min through 50 ml of a silver nitrate solution of 10 mol/l concentration at a constant temperature of 20°C. The iodine concentration at the outlet changed with time as shown in FIG. 1. The percentage of the iodine removed from the gas stream, at the time when the total volume of gas passed was 26 l, was 99.885%. This value may be converted to the decontamination factor of $DF = 6.7 \times 10^3$ ($DF = \text{iodine concentration at the inlet} / \text{iodine concentration at the outlet}$). The concentration of residual silver ion in the solution after breakthrough was 0.005 ppm or less. This means that more than 99.9977% of the silver initially present in the solution was effectively utilized.

Example 2.

Simulated DOG gas, containing 200 ppm of iodine, 2000 ppm of nitrogen dioxide, and 5000 ppm of water, was allowed to pass at a rate of 0.5 l/min through silver nitrate solutions of 10, 50 and 100 mol/l. The iodine concentrations in the gas measured at the outlet showed time variations as shown in FIG. 2. This figure shows that the total amount of iodine absorbed is nearly proportional to the concentration of silver nitrate. The percentage of silver utilized effectively was 99.9977% or greater in every case. Comparison between Example 1

and the experiment of 10m mol/l in Example 2 indicates that the presence of NO_x in the gas produces no appreciable effect on the absorption of iodine.

ment of insoluble iodine compounds by bringing the said mixture gas or vapor into contact with a solution containing silver ions.

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Example 3.

An experiment was carried out under the same experimental conditions as in Example 2 using a solution containing 4 mol/l nitric acid and 50 mmol/l silver nitrate. The iodine concentration in the treated gas changed with time as shown in FIG. 3 and a comparison with the case of 50m mol/l in Experiment 2 indicates that the absorption of iodine is hardly affected by the nitric acid in the solution. This result also suggests that the effect of nitric acid, which may be produced as a result of the absorption of nitrogen dioxide in water as shown by the $3\text{NO}_2 + \text{H}_2\text{O} = 2\text{HNO}_3 + \text{NO}$, would be small.

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Example 4.

An experiment was carried out using a silver sulfate solution with a concentration of 12.5m mol/l under the same experimental conditions as in Example 2. The iodine concentration in the gas at the outlet changed with time as shown in FIG. 4. This shows that the silver sulfate solution is able to remove iodine as effectively as a silver nitrate solution. The concentration of residual silver ion after breakthrough was below 0.05 ppm. This is equivalent to a percentage of silver utilization of 99.998% or greater.

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In conclusion, from the foregoing, it is apparent that the present invention provides a novel method for the removal of iodine and iodine compounds from mixture gases or vapors using a solution containing silver ions, having the foregoing enumerated characteristics and advantages.

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It is to be understood that the invention is not to be limited to the exact details of operation, or to the exact compounds, composition, methods, procedures, or embodiments shown and described, as modifications and equivalents will be apparent to one skilled in the art, and the invention is therefore to be limited only by the full scope which can be legally accorded to the appended claims.

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Claims

A method for the removal of iodine from mixture gas or vapor characterized in that iodine is removed from a mixture gas or vapor as a sedi-

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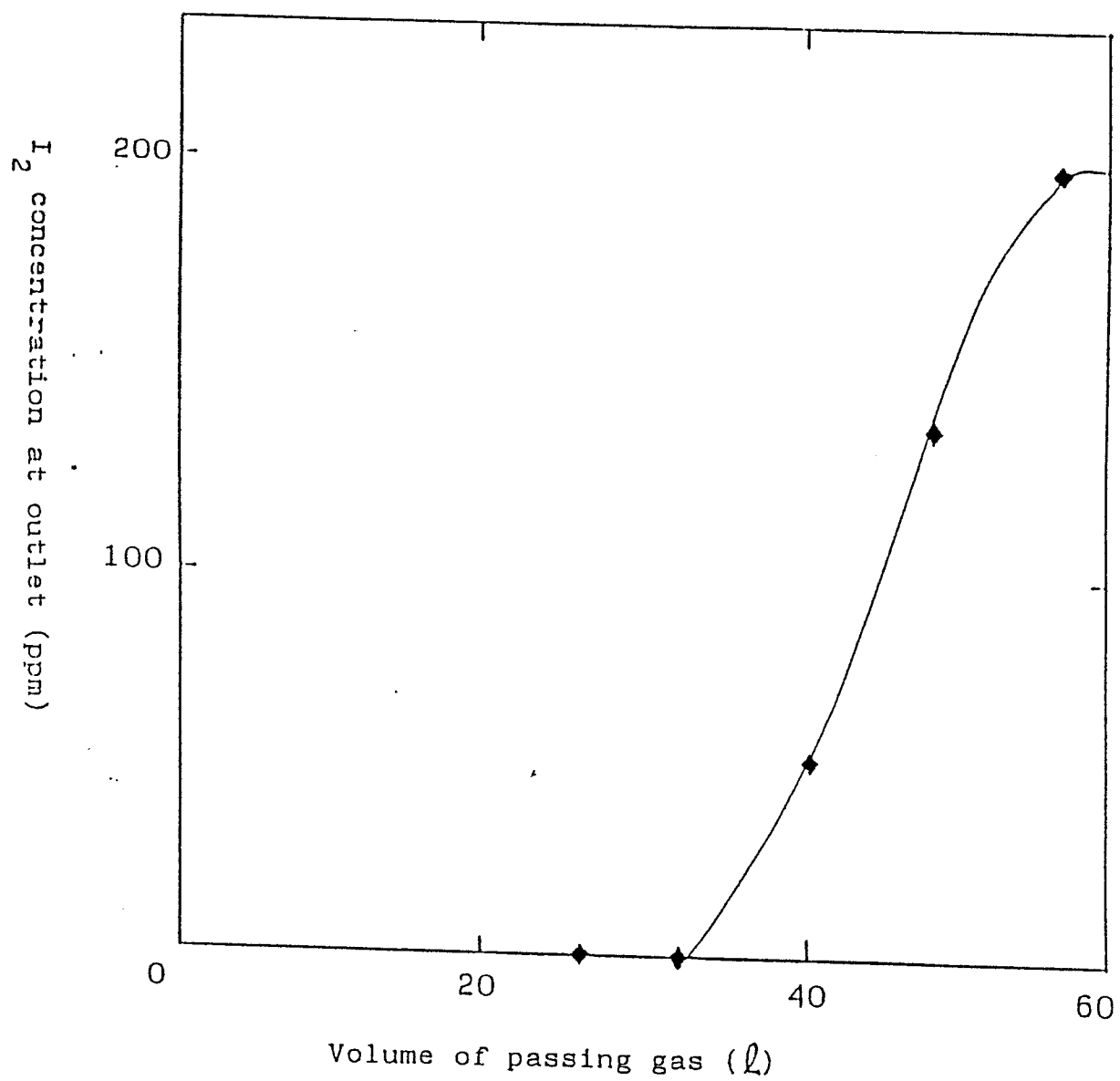


FIG.1- Breakthrough Curve of Iodine

50 ml solution (10 mmol/l- AgNO_3)

I₂ concentration at inlet = 200 ppm

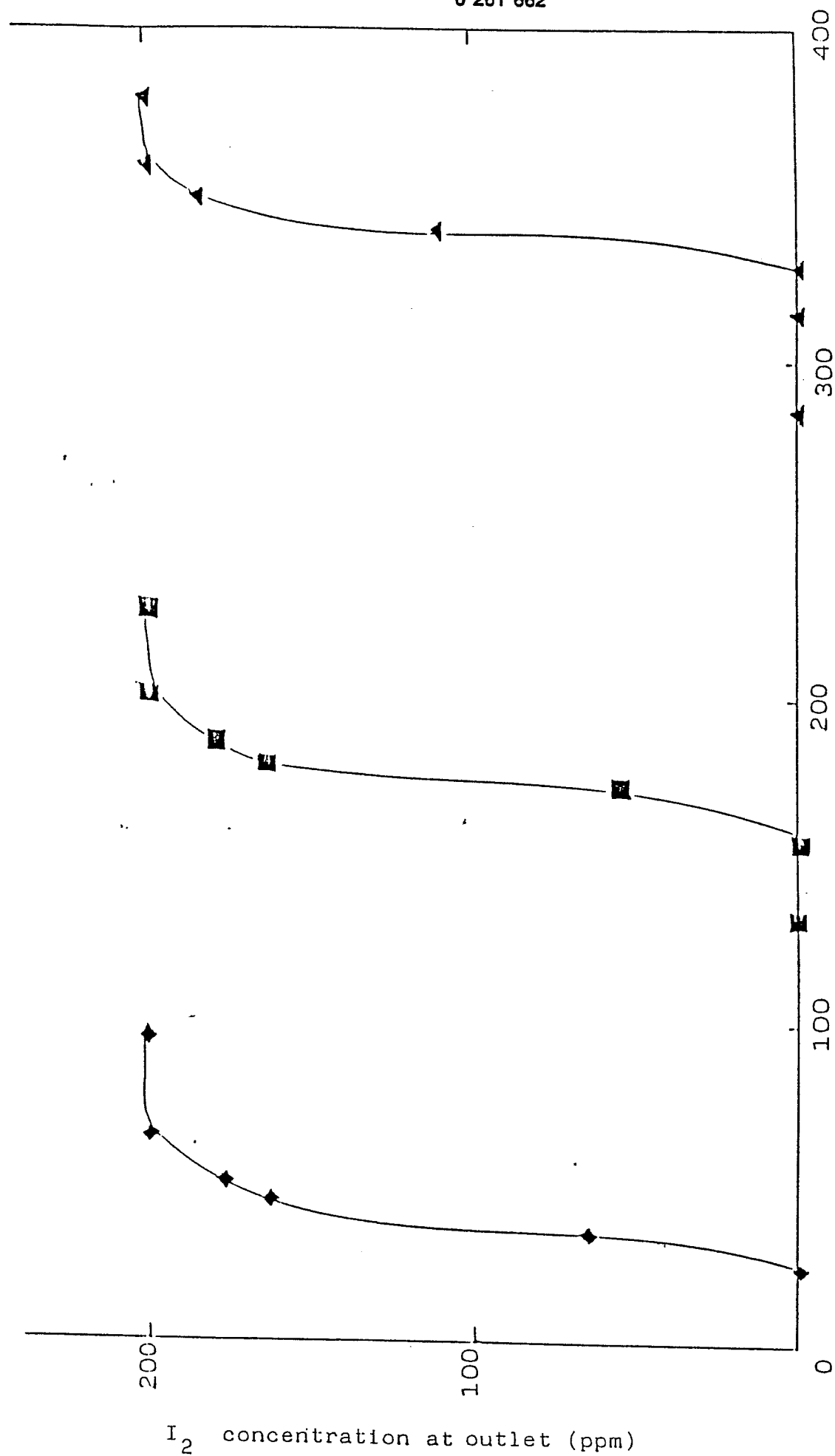


FIG. 2 - Breakthrough Curve of Iodine (effect of concentration)

50 ml solution (AgNO_3)

I_2 concentration at inlet = 200 ppm

◆ : 10 mmol/l ■ : 50 mmol/l ▲ : 100 mmol/l

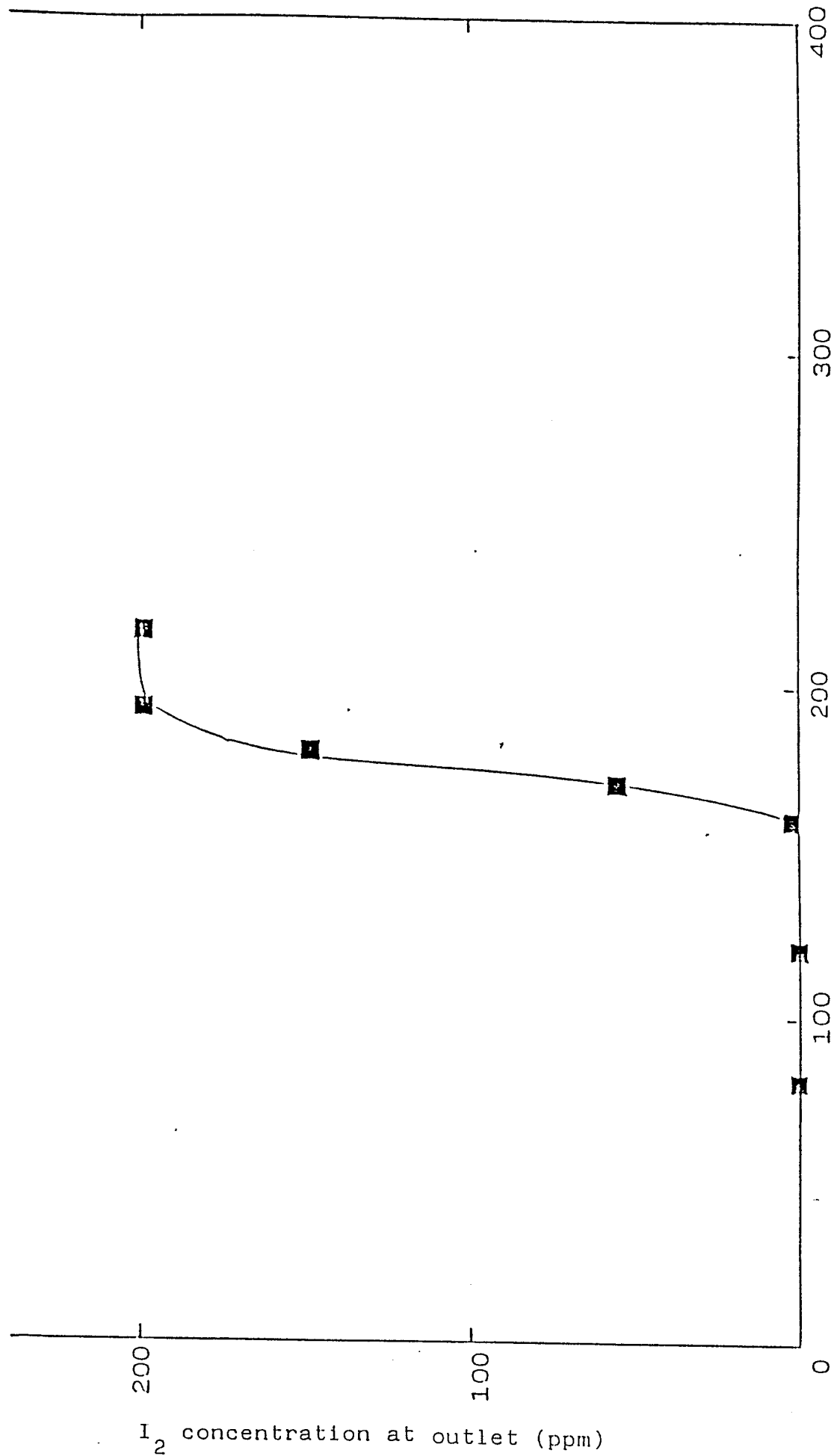


FIG. 3 - Breakthrough Curve of Iodine (effect of HNO_3)
50 ml solution (50 mmol/l- $AgNO_3$, 4 mol/l- HNO_3)
 I_2 concentration at inlet = 200 ppm

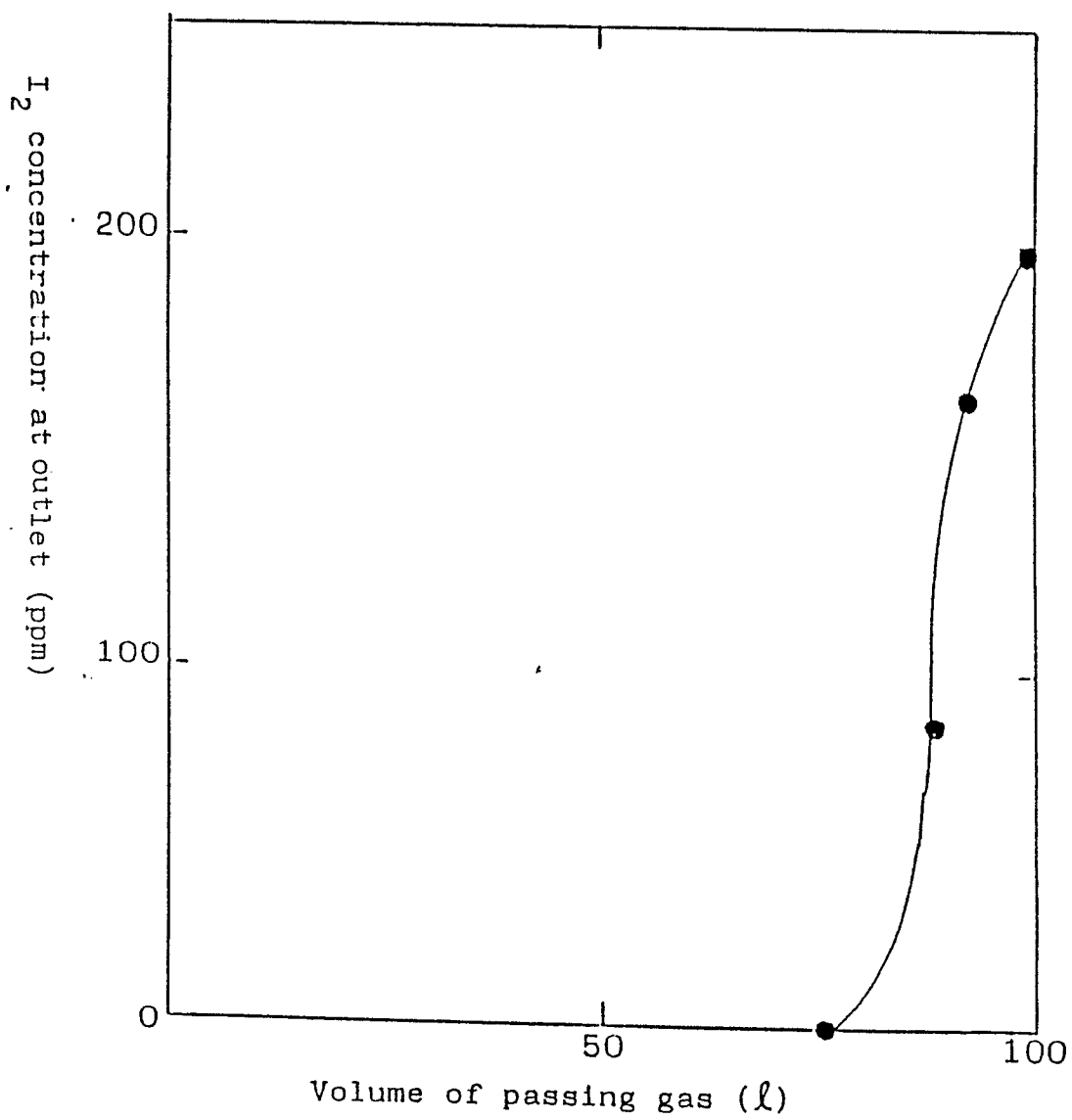


FIG.4 - Breakthrough Curve of Iodine
50 ml solution (12.5 mmol- AgSO_4)
I₂ concentration at inlet = 200 ppm