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REDUCTION OF FERRIC IRON BY SO_2 WITH HEAT OR SO_2 WITH ACTIVATED CARBON

B. H. LUCAS AND G. M. RITCEY

EXTRACTION METALLURGY DIVISION

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Technical Bulletin TB 107

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REDUCTION OF FERRIC IRON BY SO_2 WITH HEAT OR SO_2 WITH ACTIVATED CARBON

by

B.H. Lucas* and G.M. Ritcey**

SYNOPSIS

In a liquid-liquid system for the separation and recovery of individual rare earths, co-extraction of ferric iron is a serious problem. This study was done to determine whether the problem could be solved by converting the iron to the ferrous state, as opposed to precipitating the ferric iron to remove it from solution. In the precipitation of ferric iron, some co-precipitation of rare earths occurs. A synthetic iron solution, and a uranium barren solution containing 3.17 g Fe^{+2}/l and 0.34 g Fe^{+3}/l, were used in the test work.

The ferric iron in the barren solution was reduced by 90% at 90°C in 31 minutes by addition of twice the stoichiometric amount of SO_2. An alternate method used 1.5 times the stoichiometric amount of SO_2 at room temperature and 15 g/l activated carbon; retention time was 15 minutes. All of the test work was carried out in an oxygen-free system. On the basis of this work the activated carbon-SO_2 method was the more economical. Measurement of the oxidation potential can be used as a method of control.

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Bulletin technique TB 107

Direction des mines

RÉDUCTION DU FER TRIVALENT PAR SO_2 SOUS L'ACTION DE LA CHALEUR OU PAR SO_2 EN UTILISANT DU CARBONE ACTIVÉ

par

B. H. Lucas* et G. M. Ritcey**

RÉSUMÉ

Dans un système liquide-liquide pour la séparation et la récupération individuelle des terres rares, la coextraction du fer trivalent présente de sérieuses difficultés. Cette étude a été menée en vue de déterminer s'il était possible de résoudre le problème en ramenant le fer à l'état bivalent plutôt qu'en précipitant le fer trivalent pour le retirer de la solution. Dans la précipitation du fer trivalent, une solution de fer synthétique et une solution pauvre en uranium contenant 3.17 g Fe^{+2}/l et 0.34 g Fe^{+3}/l ont été utilisées dans les essais.

Le fer trivalent de la solution pauvre en uranium a été réduit dans une proportion de 90 p. 100 en 31 minutes, à une température de 90°C, par l'addition du double de la quantité stoechiométrique de SO_2. Une autre méthode a consisté à utiliser 1-1/2 fois la quantité stoechiométrique de SO_2 à la température ambiante et 15 g/l de carbone activé; la période de rétention a été de 15 minutes. Tous les essais ont été effectués en l'absence d'oxygène. En se fondant sur les résultats de ces essais, les auteurs concluent que la méthode au carbone activé et au SO_2 est la plus économique. La mesure du potentiel d'oxydation peut être utilisée comme moyen de contrôle.

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INTRODUCTION

The sulphuric-acid barren solution from a uranium recovery circuit contains ferric iron, the amount depending upon the leaching conditions employed. Subsequent processing by solvent extraction, for the by-product recovery of rare earths or other metals present in this barren solution, would be a problem because of the possible co-extraction of ferric iron with the metal of interest. It has been found by the authors (1), in a study aimed at the recovery of rare earth elements contained in a barren solution from a plant in Elliot Lake, Ontario, that up to 35% of the ferric iron present is extracted with the rare earths in one stage when alkylphosphoric acids are used as extractants. Ferrous iron, by contrast, has less affinity for di-2-ethylhexyl phosphoric acid than ferric iron, and, therefore, the trace amount of ferrous iron that does extract is readily removed by dilute acid scrubbing of the loaded solvent prior to rare earth recovery. The purpose of this investigation was to remove the problem posed by the presence of ferric iron, by developing a method for the reduction of ferric iron to the more easily handled ferrous state prior to solvent extraction. The precipitation of ferric iron prior to solvent extraction is inefficient, since some co-precipitation of rare earths occurs.

According to Treadwell (2), it is possible to reduce the ferric iron in a "moderately acid solution" by adding sulphurous acid in excess and bringing the solution to the boiling point. Roaster gases containing SO_2 were used for "conditioning" mine waters by the Cerro de Pasco Corporation (3). Small-scale experiments, in which mine waters were contacted with roaster gases containing about 9% SO_2 in stoichiometric proportions, showed that most of the ferric iron could be reduced in a simple scrubber system. The chemistry was as follows:

$$Fe_2(SO_4)_3 + SO_2 + 2H_2O \longrightarrow 2\ FeSO_4 + 2H_2\ SO_4 \quad .. \quad [\text{Eq. } 1]$$

In this Cerro de Pasco work it was found that a "relatively low acidity" assisted the reaction. Also, low oxygen concentration was essential; otherwise the auto-oxidation reaction (Equation 2) took place:

$$2\ Fe\ SO_4 + SO_2 + O_2 \longrightarrow Fe_2\ (SO_4)_3 \quad .. \quad [\text{Eq. } 2]$$

The Cerro de Pasco Corporation also found that pyrrhotite was an effective reducing agent for ferric iron (3). In pilot-plant tests, when mine waters containing ferric iron were left in contact with lump pyrrhotite for three hours, all of the iron was reduced to the ferrous state.

Borrowman and Bridges (4), reporting on a study of the solvent extraction of thorium and yttrium, reviewed from the literature three different methods for the reduction of ferric iron. The first method used metallic iron (5) (6), which, however, would double the ferrous content of the liquor, thus promoting solvent extraction of the ferrous iron. In a second method, sodium hydrosulphide was used (7). The third method, which they adopted, consisted of hydrolysis (8) followed by SO_2 reduction using activated carbon as a catalyst (9) (10).

In practice, they heated the solution to 180°C and precipitated two-thirds of the iron. The precipitate contained iron, sulphate, phosphorus, and titanium. In a second step, the filtered solution, containing 6 g/l iron, mostly in the ferric state, was treated with SO_2 and 40 g/l activated carbon for 15 minutes. The electromotive force of the reduced solution was about -0.2 volt, using platinum versus calomel electrodes.

In view of the studies already discussed in the literature, it was decided to investigate two methods reported to be effective for reducing soluble ferric iron. This technical bulletin describes the results obtained on a synthetic solution and on a plant barren solution from Elliot Lake, Ontario, when reduction was done using both SO_2 alone at elevated temperatures, and SO_2 with activated charcoal as a catalyst at room temperature.

PROCEDURE

Synthetic feed solutions containing ferric and ferrous sulphate were made up with reagent-grade chemicals and distilled water. The Elliot Lake plant liquor used in the work was an ion-exchange barren solution from the plant of Denison Mines Limited. pH adjustment was effected by the addition of ammonium hydroxide or sulphuric acid. Sulphur dioxide was added to the tests, either as a gas directly from laboratory bottles or as an aqueous solution.

In most of the tests, two-litre volumes of feed were placed in a three-litre reaction kettle which was heated by a Glas-col heating mantle. The solution was agitated by a mechanical stirrer rotating at 1000 rpm. A two-inch diameter turbine impeller was used. A diagram of the test apparatus is shown in Figure 1.

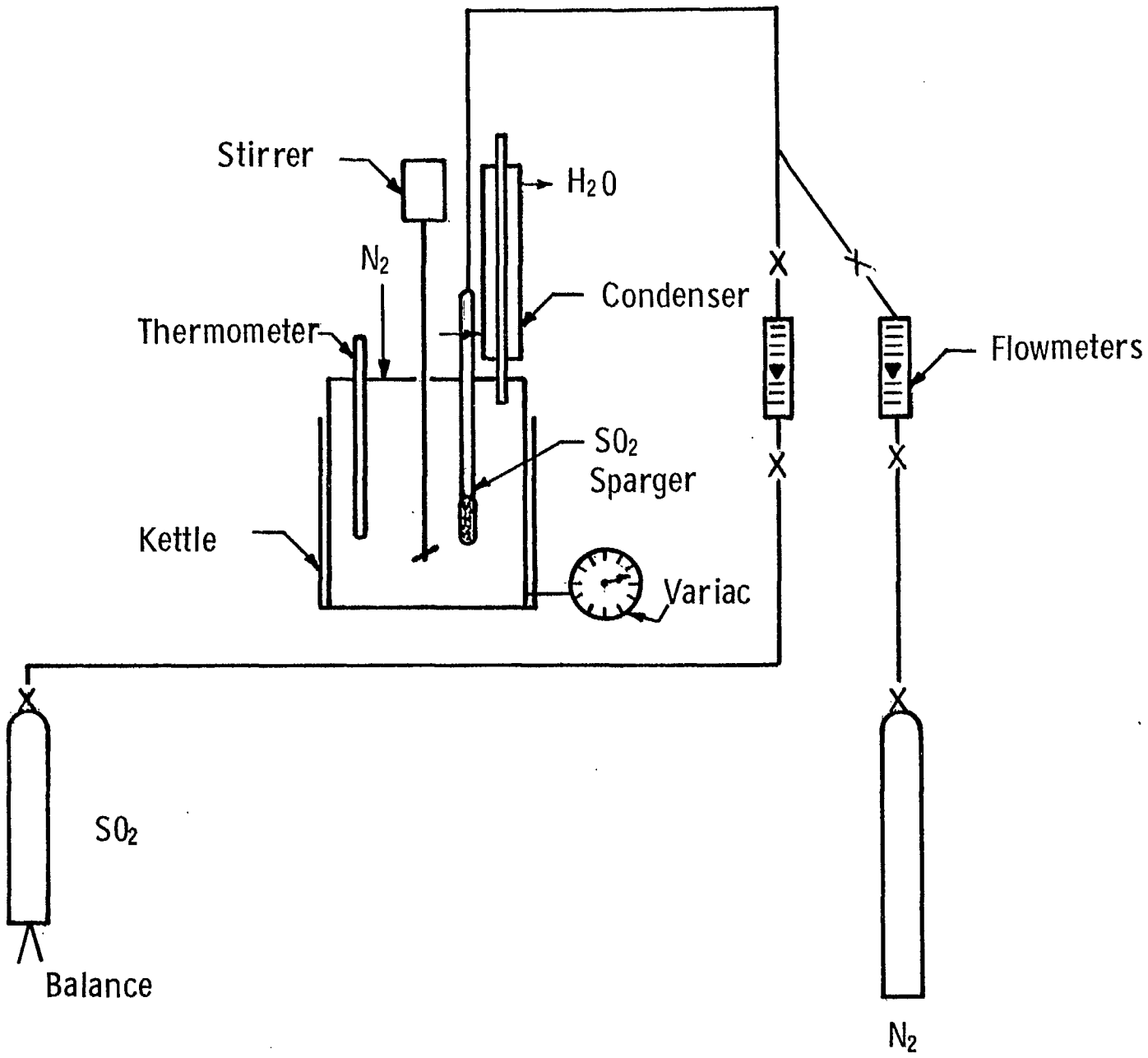

Figure I. Equipment Arrangement for SO_2 Reduction Tests.

A small flow of N_2 to purge the oxygen was maintained over the solution throughout each test, unless otherwise indicated. When the test solution was at the desired temperature, SO_2 was metered into the solution through a coarse fritted-glass sparger. Fifty-millilitre samples were taken at various increments of time (depending on the test), filtered if necessary, and assayed for ferrous and ferric iron.

The activated carbon used as a catalyst in some of the reduction tests was obtained from the Pittsburgh Coke and Chemical Company, and went under the company's designation of Type CAL 12 x 40 mesh. In the tests in which activated carbon was used, half-litre volumes of Denison barren solution were used as feed and the SO_2 was added as an aqueous solution.

The potassium dichromate method was used for the iron determination. Prior to analysis, the sample solution was purged with N_2 to remove excess SO_2. Oxidation-reduction measurements by platinum-colomel electrodes were also taken in some of the tests.

RESULTS

It is known that the concentration of any one rare earth in a typical barren liquor from an Elliot Lake uranium plant is in the order of 0.05 g/l. Also, it is desirable, in the recovery of rare earths by solvent extraction with di-2-ethyl hexyl phosphoric acid, to have the ferric iron concentration about the same as the rare earth concentration to minimize the extraction of ferric iron in preference to rare earths (1). This means that, when treating a solution containing 4g Fe^{+3}/l, it would be necessary to convert about 99% of the ferric to ferrous iron whereas with Denison barren solution (0.34 g Fe^{+3}/l) a conversion of only 90% is required.

The test work was done in two stages. In the first stage, synthetic ferric sulphate solutions were reduced in experiments aimed at determining the effect of temperature and pH on the rate of the reduction reaction. In the second phase, Denison barren solution was reduced in experiments aimed at the development of a method suitable for conducting the reduction step.

Reduction of Synthetic Ferric Sulphate Solution

Test work to determine the effect of temperature on the reduction reaction rate was done on a synthetic solution analyzing 4 g Fe^{+3}/l at temperatures of 50, 70 and 90°C and a feed pH of 2, the approximate pH value of Elliot Lake uranium barren solutions. Pure SO_2 was delivered through a sparger at about 0.5 g/min (Figure 1). The results in Figure 2 show that an increase in temperature from 50°C to 70°C had little effect on the rate of conversion, whereas a temperature increase from 70°C to 90°C almost halves the time required to bring about a conversion of ferric to ferrous of 99% (0.035 g Fe^{+3}/l). Some iron hydrolysis occurred initially but cleared up as the pH was reduced by SO_2 addition.

The effect of pH on the rate of reduction was then investigated in a series of tests carried out on a synthetic solution analyzing 4 g Fe^{+3}/l at the intermediate temperature of 70°C, and at feed solution pH levels of 1.5, 2.0 and 2.5. Pure SO_2 was delivered at about 0.5 g/min. Although Figure 3 shows that a pH of 1.5 resulted in the most rapid rate of reduction initially, 99% conversion of Fe^{+3} to Fe^{+2} was obtained in the pH 2 solution at essentially the same retention time as was obtained on the pH 1.5 solution.

Reduction of Denison Barren Solution

The conditions selected for the first ferric-reduction work on Denison barren solution were: 90°C, 0.7 g SO_2/min, and a normal barren solution of pH of 2.2. The liquor analyzed 3.17 g Fe^{+2}/l and 0.34 g Fe^{+3}/l. The ferric iron was reduced by 90% in 31 minutes. The amount of SO_2 delivered in this test was based on the amount used in the work where synthetic feed solutions were employed, although it was realized that the amount of SO_2 used was uneconomic. The amount of SO_2 used was 72 times the SO_2 required by the stoichiometry of the reaction (Equation 1). The minimum quantity of SO_2 necessary for efficient reduction of the ferric iron in the Denison barren solution was therefore the subject of the subsequent study.

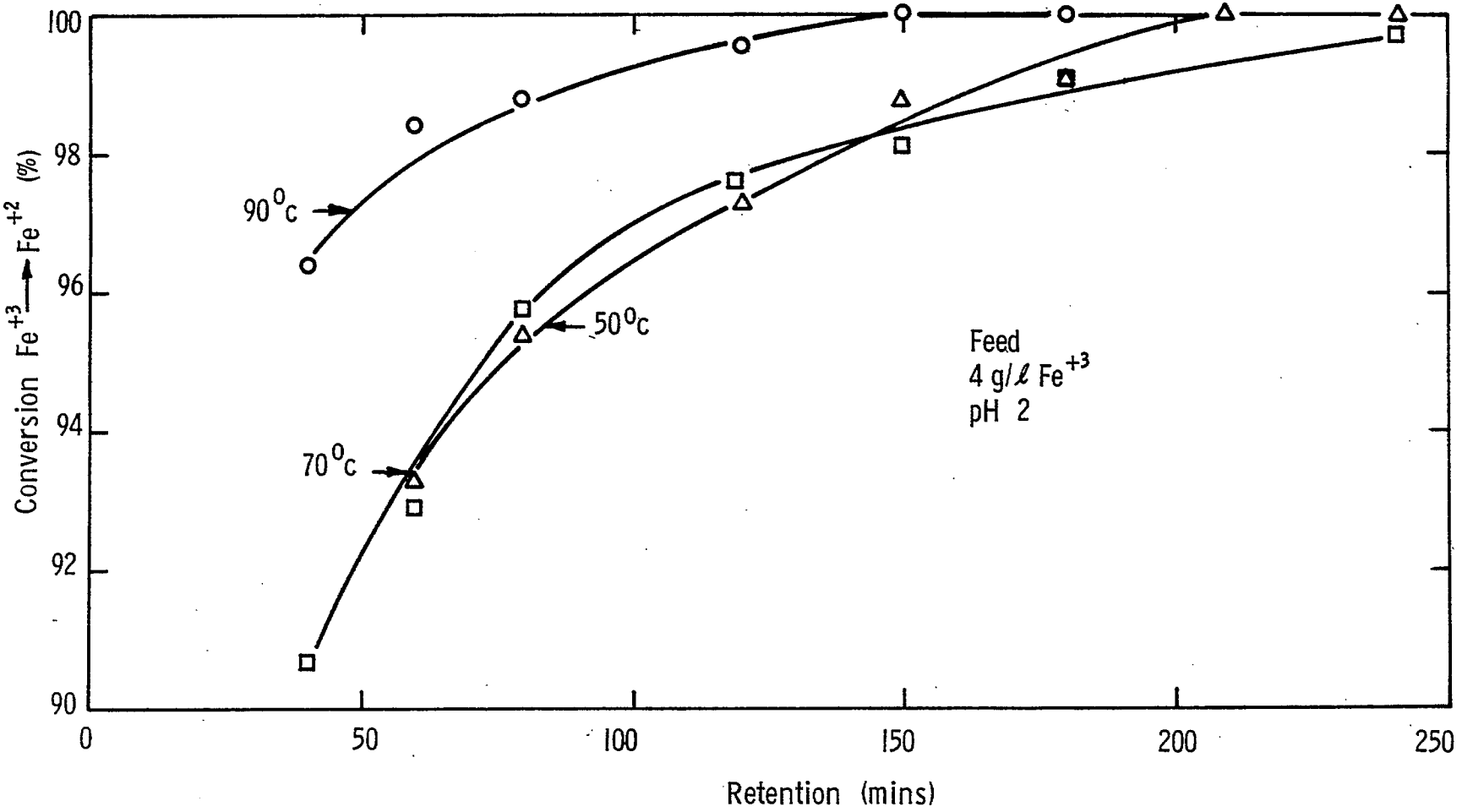

Figure 2. Effect of Temperature on Reduction of Ferric Iron by SO_2.

The conversion efficiency obtained when stoichiometric and twice-stoichiometric quantities of SO_2 were used was investigated. Figure 4 shows that twice the stoichiometric SO_2 gave 90% conversion in 31 minutes. The pH of the solution when 90% of the ferric iron was converted to Fe^{+2} was 1.95, which is an advantage since the desirable pH for the solvent extraction step is 2. A light precipitate, amounting to 0.05 g/l, formed and it was found that it consisted of iron, lead, and thorium. In the previous work on synthetic solutions, no precipitation had occurred at 50°C and 70°C. The possibility of decreasing the temperature to avoid precipitation was then investigated.

To determine the effect of temperature on the rate of reduction of Fe^{+3} to Fe^{+2} in Denison plant solutions and on the formation of a precipitate at pH 2.2, tests using twice-stoichiometric SO_2, added as an aqueous solution, were carried out at 50°, 70° and 90°C. The results are shown in Figure 5. There was a trace amount of precipitate at 70°C, but the time for conversion of ferric to ferrous iron was increased to over 200 minutes from the 31 minutes needed at 90°C. There was no precipitate formed at 50°C, but the conversion efficiency did not exceed 75%.

In another test at 70°C, the SO_2 used was increased to the equivalent of 2.5 times the stoichiometric amount, with the result that complete conversion took place in 180 minutes. A precipitate weighing 0.05 g/l formed.

It was of interest to see what effect increasing the ferric content of the uranium barren solution would have on the rate of conversion of ferric to ferrous iron. The tests were carried out at 70°C with an SO_2 addition equivalent to twice the stoichiometric amount, and at a pH of 2.2. The ferrous content of the barren solution was about 3 g/l, while the ferric content was increased up to 10 g/l by the addition of various amounts of $Fe_2(SO_4)_3$.

Figure 6 shows that when the initial Fe^{+3} to Fe^{+2} ratio was 0.77 or less (2.2 g Fe^{+3}/l), 90% of the ferric iron was converted in 3 hours or less. However, at ratios above 1.0, 90% conversion was not obtained with the amount of SO_2 used in these tests.

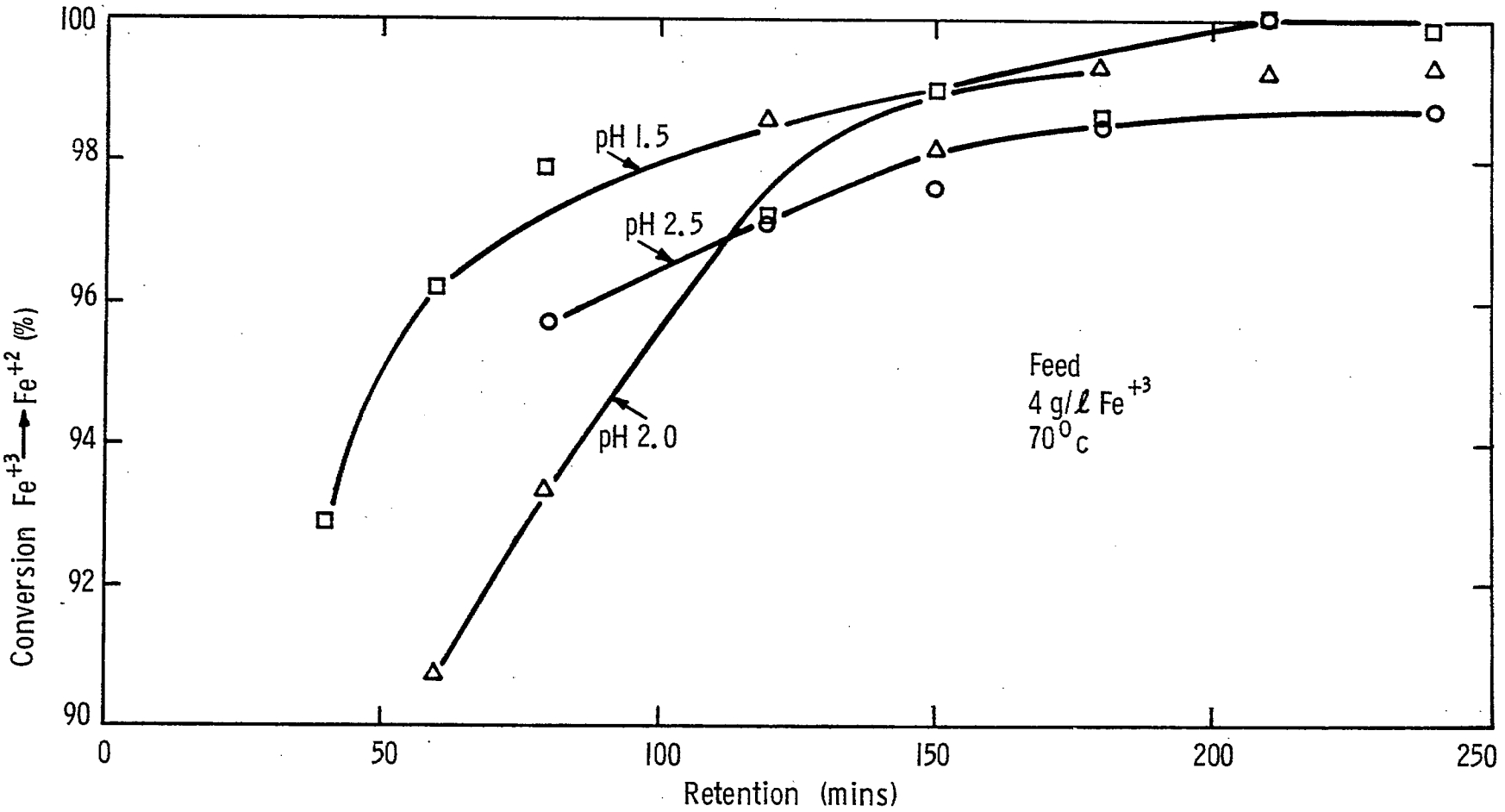

Figure 3. Effect of pH on the Reduction of Ferric Iron by SO_2.

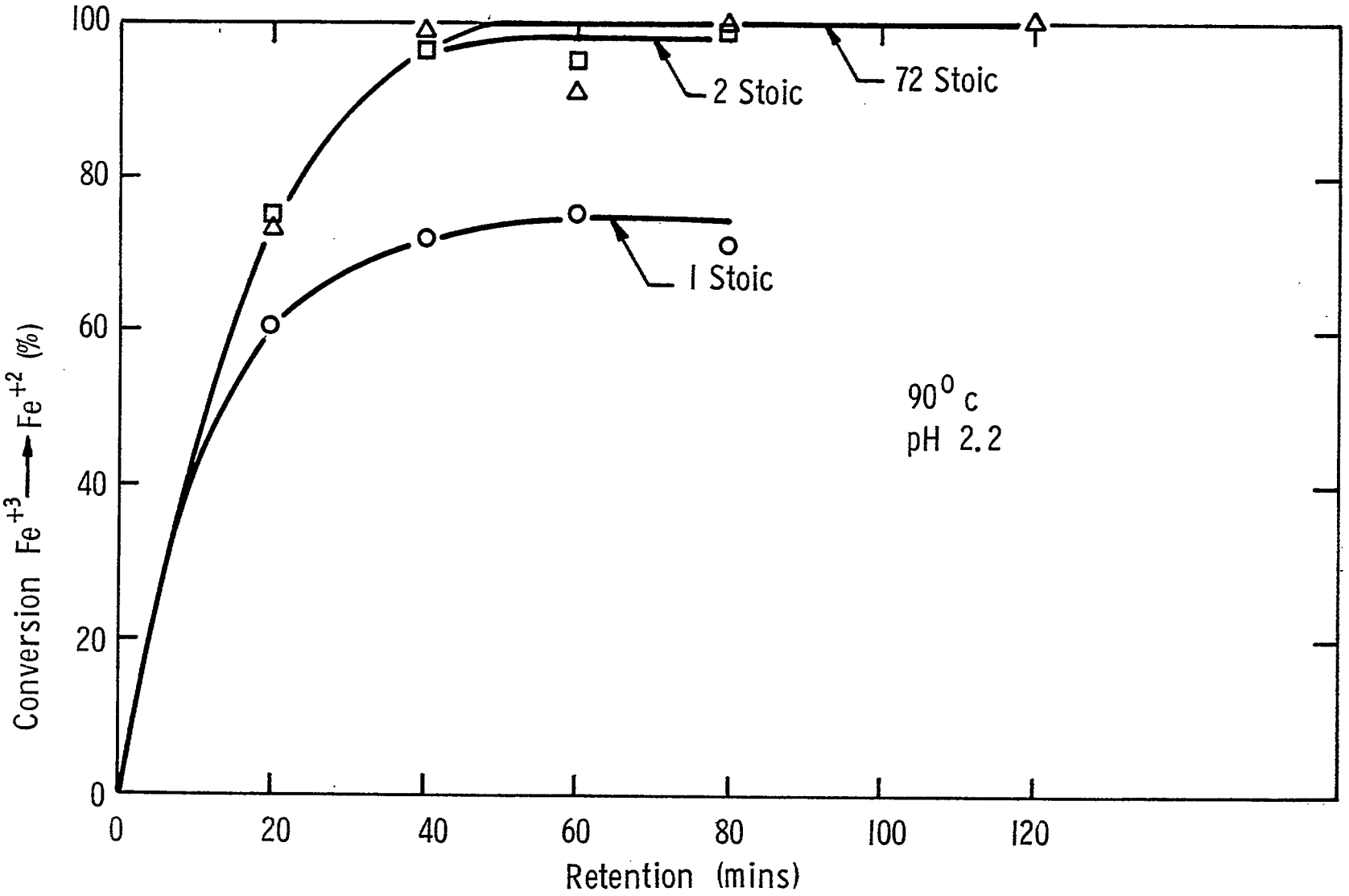

Figure 4. Effect of Amount of SO_2 in Reducing Ferric Iron in Barren Solution.

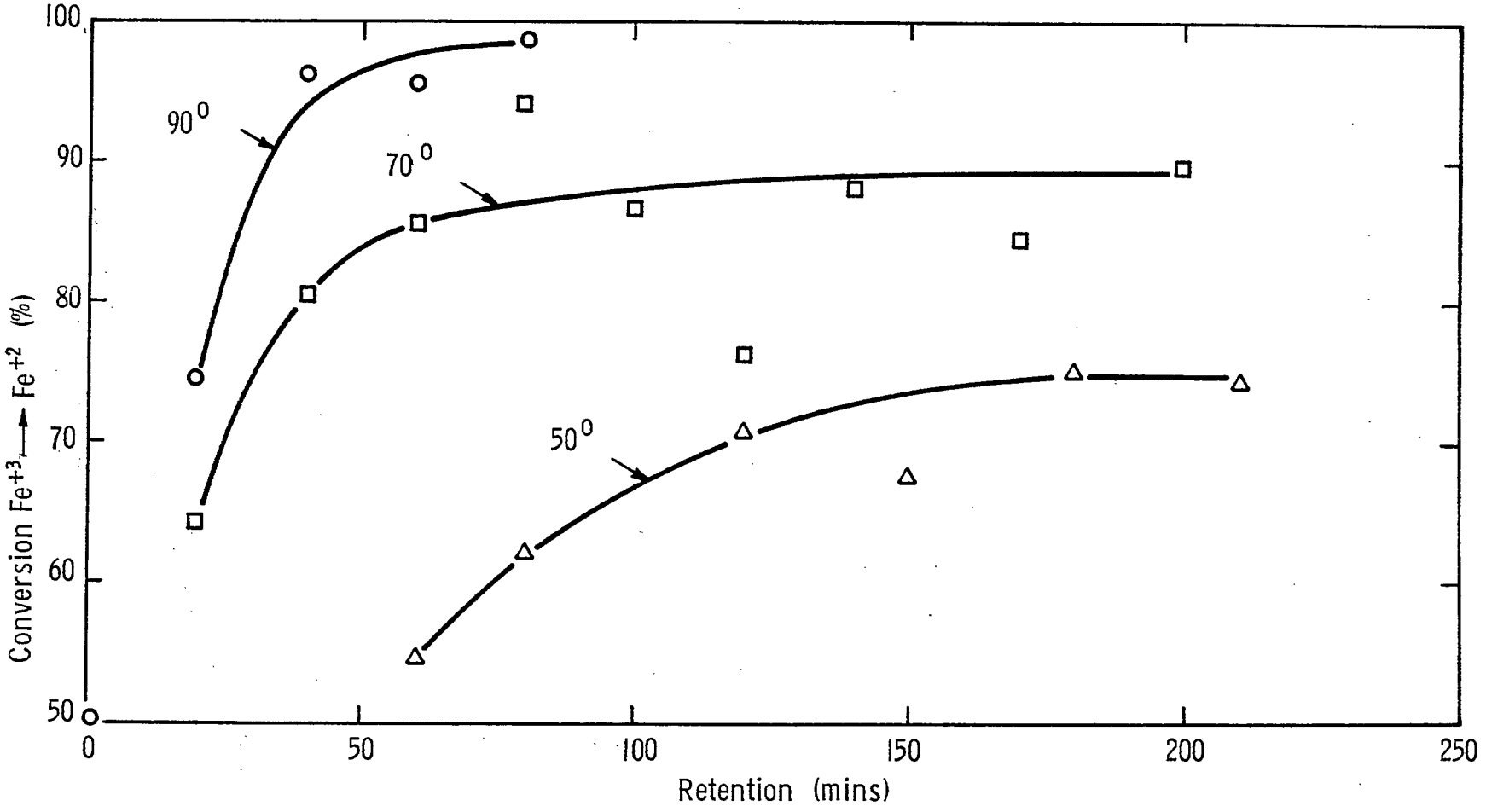

Figure 5. Effect of Temperature at 2-Stoic. SO_2 on Reduction of Ferric Iron in Barren Liquor.

A trace amount of precipitate formed when normal barren solution was treated, but the amount of precipitate increased as the ferric iron content increased so that, at 10 g Fe^{+3}/l, 6.55 g of precipitate formed per litre.

Borrowman and Bridges (4) were able to completely reduce with SO_2 an aqueous ferric sulphate solution containing about 6 g Fe^{+3}/l at room temperature, when activated charcoal was added to the solution as a catalyst. Consequently, a few tests were carried out to compare the conversion rate obtained with the Borrowman and Bridges technique and the rate obtained when using SO_2 alone at a temperature of 90°C (Figure 5).

In this work, minus 12 plus 40-mesh activated carbon was used. The SO_2 was added as an aqueous solution. Twenty grams per litre of activated carbon was mixed with 500 millilitres of Denison barren solution at room temperature, with no SO_2 added. It was found, under these conditions, that 50% of the ferric iron was reduced after 30 minutes. The test was repeated under the same conditions but with SO_2 added in an amount equal to 2.2 times the stoichiometric amount, with the result that 91.5% of the ferric iron was reduced in 15 minutes.

A series of tests was then done in which various additions of SO_2 were investigated. When using 1.1 times the stoichiometric amount of SO_2 and fresh carbon, 92.2% of the ferric iron was reduced in 15 minutes. Upon repeating the test with the same carbon, only 75.8% of the ferric iron was in the ferrous form in 15 minutes. With 1.5 times the stoichiometric amount of SO_2, and fresh carbon, it was found that 94.1% of the ferric iron was in the ferrous state after 15 minutes. Upon repeating the test with the same carbon, 93.4% of the ferric iron was reduced in 15 minutes.

With 1.5 times the stoichiometric amount of SO_2, the amount of activated carbon necessary to obtain efficient conversion was then checked. At 10 g/l carbon, 88% of the ferric iron was reduced in 45 minutes; at 15 g/l carbon, 97.2% of the ferric iron was reduced in 15 minutes. It was concluded from this work that 15 g/l activated carbon, along with 1.5 times the stoichiometric amount of SO_2, would convert efficiently the ferric iron in the Denison barren solution to ferrous iron at room temperature..

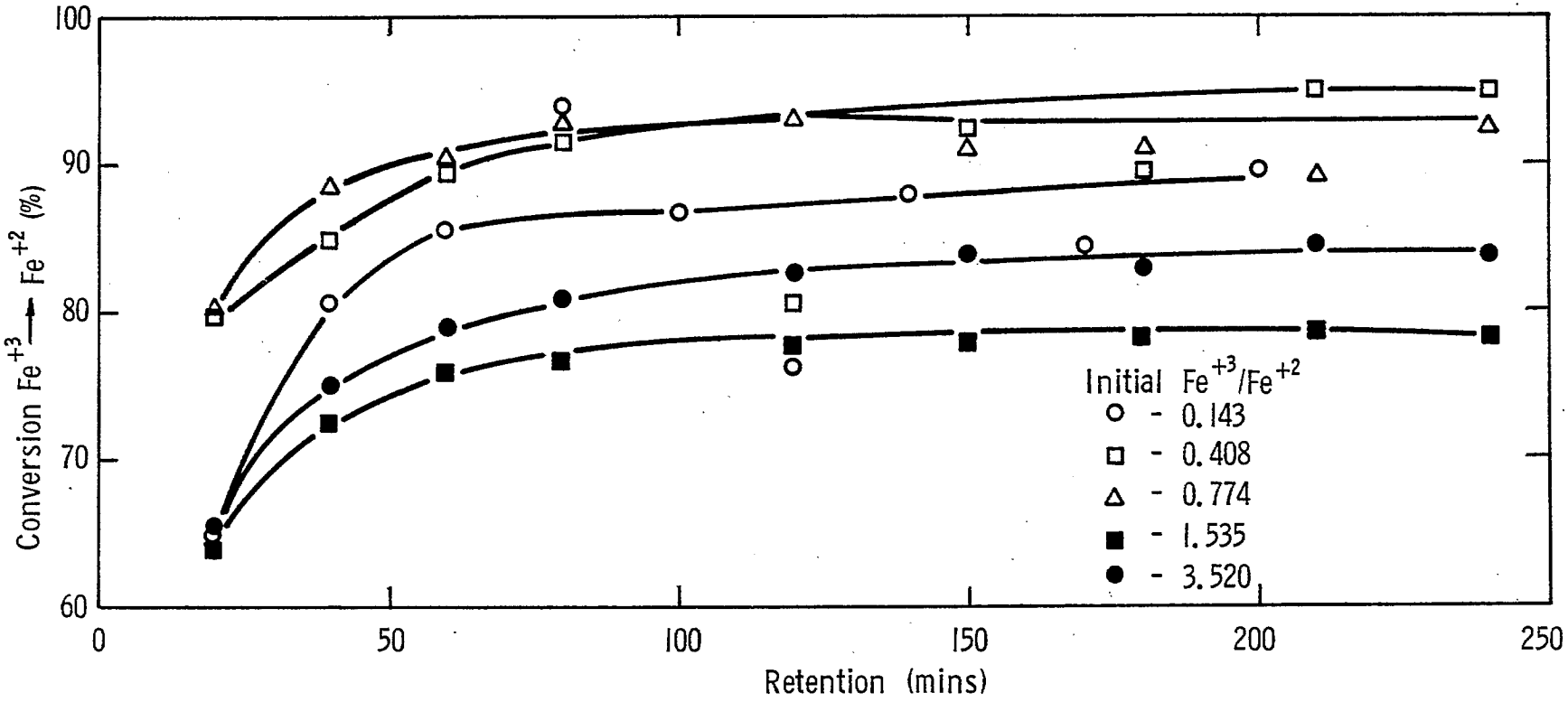

Figure 6. Effect of Initial Fe^{+3}/Fe^{+2} Ratio on Reduction Rate of Ferric Iron in Barren Liquor.

A test using the best activated carbon-SO_2 conditions was carried out, in which the conversion of the ferric iron was monitored by electromotive force readings as well as by iron analyses (Figure 7). In 15 minutes 99% of the ferric iron was reduced, and at the 30-minute mark 100% conversion was accomplished. The oxidation-reduction potential of the carbon slurry, -0.2 volt, was the same as reported by Borrowman and Bridges (4).

DISCUSSION

The reduction of ferric iron by SO_2 occurred under conditions as indicated by Treadwell (2). The results are also in some agreement with those obtained by the Cerro de Pasco Corporation (3) concerning "relatively low acidity" and the elimination of oxygen. Our work on oxygen is incomplete, since no work was done to establish the tolerable level of oxygen in the atmosphere above the reduction reaction. Inasmuch as the Cerro de Pasco data were not obtained, it is not known how low a ferric content they developed when using stoichiometric additions of SO_2. They may have to use more than the stoichiometric amount of SO_2 if they wish to reach a residual value of 0.035 g Fe^{+3}/l, as in the case of this test work. The activated carbon-SO_2 results agree with those obtained by Borrowman and Bridges (4).

The conditions necessary to reduce the ferric iron in the Denison barren solution by SO_2 and heat are: twice the stoichiometric amount of SO_2, a retention time of 31 minutes, a temperature of 90°C, and a virtual absence of oxygen. In comparison, the conditions for the activated carbon-SO_2 system are: 15 g/l carbon, 1.5 times the stoichiometric amount of SO_2, a 15-minute retention time at room temperature, and the virtual absence of oxygen.

It is possible that the oxygen levels in SO_2 roaster gases are sufficiently low to provide the inert atmosphere desired. The activated carbon-SO_2 system takes less SO_2 than the SO_2-high temperature system, but would incur the extra cost involved in the use of carbon. Only one-half the retention time is necessary, thus a smaller plant would be required. In comparing the economics of the two systems, the main differences would be found in the operating costs involved in heating the solution, in the one system, and in the carbon required for make-up, in the other.

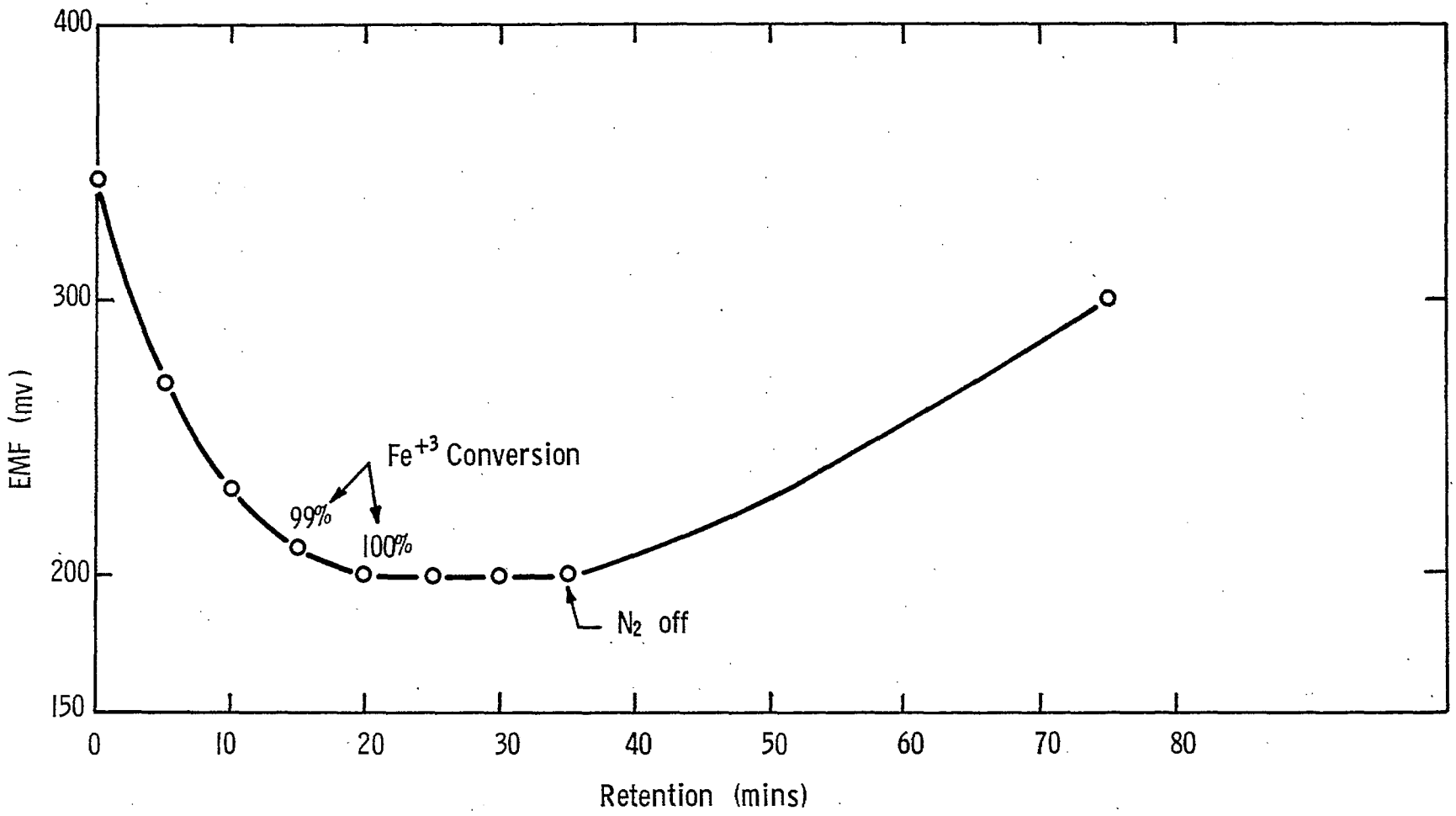

Figure 7. EMF Readings on SO_2 - Activated Carbon Reduction of Barren Solution.

In one test, using a rather extreme agitation, the carbon loss by size reduction was 0.87%. Assuming a 1% carbon loss, the cost of carbon make-up would be 9¢ per ton of solution at 30¢ per pound of carbon. Assuming that a gallon of fuel oil contains 148,000 BTU and costs 18¢ and that 50% of the heat content of the oil is utilized, it would cost 52¢ per ton of solution to heat the solution from 64°F to 194°F (90°C). At 7¢ per pound of SO_2, the costs for SO_2 to the SO_2-heat system and to the activated carbon-SO_2 system would be respectively, 2.7¢ and 2.1¢ per ton solution. Thus, the SO_2-heat cost would total 55¢, as opposed to the total cost of 11¢ for carbon replacement and SO_2.

Since this investigation was limited in scope, no economic comparison was made with current operating practices. For example, it is not known whether the carbon would become de-activated in time and require regeneration. It has also not been determined whether the precipitate which forms from the use of heat would have to be removed prior to solvent extraction. However, on the basis of the comparison made of costs, the activated carbon-SO_2 system must be considered the more economical method to reduce the ferric iron to the ferrous state.

CONCLUSIONS

Ninety percent of the ferric iron present in an Elliot Lake uranium plant barren solution, similar to that of Denison Mines Ltd., can be converted to the ferrous state in about half an hour by heating the solution to 90°C and adding SO_2 in an amount equal to twice the stoichiometric amount required. The SO_2 and heat costs would be in the order of 55¢ per ton of solution.

Alternatively, a solution of the same type as discussed above can be treated by contacting it with 15 g/l activated carbon and 1.5 times the stoichiometric amount of SO_2 for 15 minutes at room temperature. In either method the virtual absence of oxygen is necessary. The cost of SO_2 and carbon replacement in the activated carbon-SO_2 system is estimated to be 11¢ per ton of solution. The latter system is considered to be the more economical.

ACKNOWLEDGEMENTS

The assistance of Mr. K. Price and Mr. L. Fleury in the test work is gratefully acknowledged.

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