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(54) **A process for the cleaning of metallic, for example iron or steel, internal surfaces of industrial equipment.**

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Description

The invention relates to a process for the cleaning during idle periods of metallic, comprising iron or steel, internal surfaces of equipment used in the chemical industry, in which a cleaning fluid containing water, an acid and a corrosion inhibitor is pumped through the interior of the equipment at a flow rate of at least 0.5 m/s. Examples of such equipment include reactors, heat exchangers, pipes, pumps, valves distillation columns and steam boilers.

A process as mentioned above is known from the patent specification no. US-A-3,440,170. Piping systems are cleaned by causing an acid, such as hydrochloric acid or sulphuric acid, to which a corrosion inhibitor has been added, to circulate through them at a liquid flow rate given as 1 m/s. Despite the presence of a corrosion inhibitor, the surfaces to be cleaned according to this process are attacked by the acid, and that more seriously as higher flow rates are employed. An effective treatment of the surfaces to be cleaned with an acid in this fashion leads to significant concentrations of ferric ions which have a marked corrosive effect on the iron or steel wall. Corrosion by ferric ions cannot be combated adequately by the use of corrosion inhibitors such as hexamethylenetetramine, hydrazine, alkaloids and quaternary ammonium compounds and may even occur to such a degree that after the cleaning operation pitting and scoring are observed in the metal of the cleaned equipment.

Pitting and scoring are encountered especially with unalloyed and low-alloy steels which are widely used in steam boilers. The corrosion renders the metal surfaces rough, causing a reduction in flow rate of the water in the evaporator tubes of steam boilers, whereby the heat transfer is decreased and the wall temperatures in the installation locally rise.

When combinations of a nobler and a less noble metal are present in the equipment to be cleaned, an intensified corrosive attack on the less noble metal is found to occur. It is indeed possible to reduce this intensified corrosion, for instance by blanking off or removing the nobler metal from the equipment before the cleaning operation, but it will be obvious that in actual practice such a step is, to say the least, inconvenient and often impracticable.

It has been found that when steel comes into contact with a hydrochloric-acid bath which is kept in motion and which contains a corrosion inhibitor and ferric compounds, at a temperature as low as 20 °C 50% of the ferric ions are reduced within two hours to ferrous ions at the expense of the equivalent amount of steel which goes into solution. At 50 °C, a normal temperature for cleaning steam boilers, for example, this degree of corrosion is even reached within one hour. As it may take several hours to fill a fairly sizable steam boiler with cleaning fluid by means of a circulating pump, severe corrosion has already set in during the filling. It also follows that no substantial improvement can be achieved by repeated withdrawal of the cleaning acid containing the ferric ions and replacement with fresh acid, quite apart from the greatly increased cost.

US-A-3,440,170 proposes that in a cleaning fluid which is pumped around in the interior of iron or steel equipment for the removal of rust, for example, and which contains water, an acid and a corrosion inhibitor, in addition a stannous salt be dissolved and that the composition of the cleaning fluid be controlled during operation by measurement of the redox potential. In this system, the addition of fresh stannous salt, as the need arises, during operation serves as a means to keep the redox potential of the cleaning fluid below a limiting value which, when measured with a platinum electrode against a saturated calomel-KCl electrode, amounts to 280 mV. In US-A-3,440,170 the preferred stannous salt soluble in the cleaning fluid is stannous chloride and the preferred cleaning acid is hydrochloric acid.

The process described in US-A-3,440,170 has the disadvantages as that it is hardly, if at all, applicable in a great many industrialized countries, because stringent environmental requirements practically preclude the use of stannous salts, whilst the discharge of tin-containing substances is even prohibited, and b) in practice it is not efficient to transport loose stannous salt to and from the equipement to be cleaned, as well as to process used stannous salt into fresh stannous salt.

The object of the present invention is to provide an environmentally acceptable, efficient, fully controllable process for the cleaning during idle periods of metallic, for example iron or steel, internal surfaces of equipment used in the chemical industry, in such a fashion that no corrosion of the surfaces to be cleaned occurs. To achieve this goal, a process of the type mentioned hereinbefore is according to the invention characterized in that the cleaning fluid is passed through a reduction filter disposed outside the equipment, which filter substantially comprises a vessel with mutually spaced strainer discs between which a substantially metallic packing is contained in the form of roll-up mats being coiled round a core of the vessel, whereby the vessel is provided near either end with an inlet and an outlet port, respectively, for the cleaning fluid. The use of the substantially metallic (for instance, steel, iron or aluminium) packing, which is preferably steel wool with a surface-to-weight ratio of e.g. 15 m^2/kg, ensures that ferric ions formed through the action of the acid are very

effectively reduced to ferrous ions. Thus, corrosive attack on the surfaces to be cleaned is obviated in an environmentally acceptable manner. Preferably steel-wool mats are used.

One embodiment of a process according to the invention is characterized in that the redox potential is measured in a filtrate of the reduction filter.

The process according to the invention can be carried out in practice as follows. After calculation of the overall surface area to be cleaned of, for instance, a steam boiler the reduction filter is provided with a steel-wool packing having a surface area at least ten times as large. Thereupon the boiler is filled with a one-percent inhibited hydrochloric-acid solution which is circulated at room temperature, i.e. 20 °C, at a rate in m^3/h at least four times as high as that of the contents of the boiler. This procedure ensures that the iron oxides slowly pass into solution whereas the ferric compounds are quickly reduced. Then, the acid concentration is slowly raised to the requisite level, normally 4 to 5%. The outlet for draining the cleaning acid from the steam boiler (suction line circulation pump) must be disposed as low as possible, such that the hydrochloric acid, which may be rich in ferric ions, can be discharged most quickly to the reduction filter. In order to accelerate the cleaning process, the temperature of the circulating acid may, if desired, be raised to, say, 50 °C.

After the cleaning, the hydrochloric acid is neutralized with sodium hydroxide to a pH of 7 or 8, whereby sodium chloride and water are formed. In the treatment of the neutral sodium-chloride-rich waste water, the iron compounds present are quickly oxidized to ferric compounds, which does not give rise to environmental problems. As a matter of fact, the corrosion inhibitor is biologically degradable, hence also ecologically acceptable.

It is to be noted that the process according to the invention makes it possible to clean the internal surfaces of industrial equipment without any corrosive attack, when constructed in any of the following metals: steel 37; carbon steel 50-60; 1% Cr - ½% Mo steel; 5% Cr - ½% Mo steel; copper nickel 70-30; inconel; nionel; nickel; monel; hastelloy.

The invention also relates to a reduction filter suitable for use in a process according to the invention, which reduction filter is characterized in that it substantially comprises a vessel with mutually spaced strainer discs between which a substantially metalic, for example iron or steel, packing in the form of roll-up mats being coiled round a core of the vessel is contained, which vessel is provided near either end with and inlet and an outlet port, respectively, for the cleaning fluid.

A further embodiment of a reduction filter according to the invention is characterized in that the reduction filter is transportable. In consequence, the process according to the invention can be flexibly operated, for instance on board of (seagoing) vessels.

Patents abstracts of Japan, Volume 5, No. 4 (C-38) [676] dated January 13, 1981 and the Japanese patent publication No. JP-A-55131183 describe a process for removing scale adhered to a surface of metallic material by chemical washing, whereby a washing fluid is circulated through a strainer packed with granular, powdered or fibrous iron in order to reduce oxidizing, corrosive metallic ions (Fe^{3+}, Cu^{2+}, Cu^{+}) which are dissolved in the washing fluid. The strainer packed with granular, powdered or fibrous iron is disposed outside the equipment.

Chemical abstracts, Volume 103, No. 4 dated July 19, 1985, page 203, abstract No. 25764k, Columbus Ohio, United States of America discloses a process for continuous treatment of strong acid baths for descaling and pitting whereby the bath contents is circulated through a filter charged with iron shavings, thus converting ferric ions.

A reduction filter and a process according to the invention will now be elucidated further with reference to the accompanying figures 1 and 2.

Figure 1 represents a reduction filter in the form of a vessel 1 which has been made of a pressure-resistant material that is impervious to acids up to a temperature of at least 70 °C. As regards pressure resistance, it is to be noted that the vessel 1 must be capable of withstanding a pressure of at least 3 bar. To ensure durability, the vessel 1 should preferably be made in a glass fibre-reinforced acid-proof polyester.

The vessel 1 is provided with two detachable, fixed or movable strainer discs 2, 3, preferably consisting of perforated polypropylene trays, whilst fine steel-wool mats 5 have been coiled round a core 4 of the vessel 1. The cleaning fluid which contains water, an acid and a corrosion inhibitor is, after having been pumped through the interior of the equipment to be cleaned, introduced through an inlet 6 (arrow 7) into the vessel 1 and, after having been filtered, passes through an outlet 8 (arrow 9) to the interior of the equipment to be cleaned.

The vessel 1 has a drain cock 10, permitting check measurements to be carried out in the circulating cleaning fluid. By means of this drain cock 10 the cleaning fluid may be discharged, if necessary. Inside the drain cock 10 a hose may be connected for the continuous measurement of redox potentials, the determination of the non-corrosivity of the cleaning fluid and the removal of air bubbles, if any.

When the need arises to replace the steel wool 5 or to neutralize the cleaning fluid, this fluid is passed, for instance by means of a three-way cock

mounted near the inlet 6, direct through the core 4 - instead of over the steel wool 5 - and then withdrawn. The cleaning fluid is neutralized with, for instance, caustic soda or another base, whereupon it is processed by a waste-water purification plant. In actual practice, it has not been found feasible to neutralize the cleaning fluid during its passage over the steel wool 5, because in that case the fine-pored steel wool 5 would have become clogged and unsuitable for further use.

Provided that the appropriate inhibitors are used, the reduction filter removes harmful ferric, cupric, cuprous and other corrosive ions from hydrochloric acid (at concentrations of 0.5 - 15%), but also from the cleaning acids:
hydrofluoric acid (at concentrations of 0.5 - 10.0%),
sulphuric acid (at concentrations of 0.5 - 20.0%),
citric acid (at concentrations of 3.0 - 15.0%),
phosphoric acid (at concentrations of 1.0 - 10.0%),
hydroxyacetic acid (at concentrations of 1.0 - 10.0%),
formic acid (at concentrations of 2.0 - 15.0%),
sulphamic acid (at concentrations of 1.0 - 15.0%),
ethylenediaminetetra-acetic acid (at all usable concentrations),
and from mixtures of these acids or their salts.

Figure 2 affords a clear picture of the conditions that may occur during chemical cleaning of, for instance, a fouled steam boiler with inhibited hydrochloric acid, without specification of the relevant corrosion values which have been established.

When cleaning is carried out according to the process of the invention, the redox potential will be 280 mV or lower, which means no corrosion ("safe area; no attack").

Even when only 0.5 g of ferric ions per litre is present in the cleaning acid, as will occur with many known cleaning procedures by a conservative estimate (redox potentials of 300 to 400 mV), corrosion will manifest itself ("slight attack").

During cleaning tests according to the "classical" process, redox potentials of 500 mV and over were observed, which were invariably attended with serious to very severe corrosion of steel and other construction materials ("serious attack to very severe corrosion").

Claims

1. A process for the cleaning - during idle periods - of metallic internal surfaces of equipment comprising iron or steel parts, in which a cleaning fluid containing water, an acid and a corrosion inhibitor is pumped through the interior of the equipment at a flow rate of at least 0.5 m/s, whereby the composition of the cleaning fluid is controlled during operation by measurement of the redox potential, which is maintained below a limiting value and amounts to nearly 280 mV or less, when measured with a platinum electrode against a saturated calomel-KCl electrode, characterized in that the cleaning fluid is passed through a reduction filter (1) disposed outside the equipment, which filter (1) substantially comprises a vessel with mutually spaced strainer discs (2,3) between which a substantially metallic packing (5) is contained in the form of roll-up mats being coiled round a core (4) of the vessel, whereby the vessel is provided near either end with an inlet and an outlet port, respectively, for the cleaning fluid.

2. A process according to claim 1, characterized in that steel-wool mats are used.

3. A process according to claim 1 or 2, characterized in that the redox potential is measured in a filtrate of the reduction filter (1), within the filter housing.

4. A reduction filter (1) suitable for use in a process according to any one of the preceding claims, characterized in that it substantially comprises a vessel with mutually spaced strainer discs (2,3) between which a substantially metallic packing (5) in the form of roll-up mats being coiled round a core (4) of the vessel is contained, which vessel is provided near either end with and inlet and an outlet port, respectively, for the cleaning fluid.

5. A reduction filter according to claim 4, characterized in that it constitutes a removable device.

Patentansprüche

1. Ein Verfahren zur Reinigung - während Stillständen - von metallischen Innenflächen von einem Apparat aus Eisen- oder Stahlteilen, bei dem eine Reinigungsflüssigkeit, die Wasser, eine Säure und ein Korrosionsschutzmittel enthält, durch das Innere des Apparats mit einer Durchflußleistung von wenigstens 0,5 m/s gepumpt wird, wobei die Zusammensetzung der Reinigungsflüssigkeit während des Betriebs durch Messung des Redox-Potentials gesteuert wird, das unter einem Grenzwert gehalten wird und nahezu 280 mV oder weniger beträgt, wenn es mit einer Platin-Elektrode gegen eine gesättigte Kalomel-KCl-Elektrode gemessen wird, dadurch gekennzeichnet, daß die Reinigungsflüssigkeit durch einen Reduktionsfilter (1) geleitet wird, der außerhalb des Apparats angeordnet ist, wobei der Filter (1) im wesentli-

chen einen Behälter mit wechselseitig beabstandeten Siebeinsätzen (2, 3) umfaßt, zwischen denen eine im wesentlichen metallische Füllung (5) in der Form von aufgerollten Matten enthalten ist, die um einen Kern (4) des Behälters gewickelt sind, wobei der Behälter in der Nähe beider Enden jeweils mit einer Einlaß- und einer Auslaßöffnung für die Reinigungsflüssigkeit versehen ist.

2. Ein Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß Stahlwollematten verwendet werden.

3. Ein Verfahren gemäß Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Redox-Potential in einem Filtrat des Reduktionsfilters (1) innerhalb des Filtergehäuses gemessen wird.

4. Ein Reduktionsfilter (1), der für eine Verwendung in einem Verfahren gemäß irgendeinem der vorangehenden Ansprüche geeignet ist, dadurch gekennzeichnet, daß er im wesentlichen einen Behälter mit wechselseitig beabstandeten Siebeinsätzen (2, 3) umfaßt, zwischen denen eine im wesentlichen metallische Füllung (5) in der Form von aufgerollten Matten enthalten ist, die um einen Kern (4) des Behälters gewickelt sind, wobei der Behälter in der Nähe beider Enden mit jeweils einer Einlaß- und einer Auslaßöffnung für die Reinigungsflüssigkeit versehen ist.

5. Ein Reduktionsfilter gemäß Anspruch 4, dadurch gekennzeichnet, daß er eine entfernbare Einrichtung bildet.

Revendications

1. Procédé de nettoyage - lors des périodes d'inactivité - des surfaces internes métalliques d'un appareillage comprenant des parties en acier ou en fer, dans lequel un fluide de nettoyage contenant de l'eau, un acide et un inhibiteur de corrosion est pompé à travers l'intérieur de l'appareillage, à une vitesse d'écoulement d'au moins 0,5 m/s, dans lequel la composition du fluide de nettoyage est contrôlée lors de l'opération en mesurant le potentiel redox, lequel est maintenu en dessous d'une valeur limite et des quantités allant jusqu'à environ 280 mV ou moins lorsqu'il est mesuré au moyen d'une électrode de platine en opposition à une électrode saturée au calomel-KCl, ledit procédé étant caractérisé en ce qu'on fait passer le fluide de nettoyage à travers un filtre réducteur (1) disposé à l'extérieur de l'appareillage, lequel filtre (1) comprend essentiellement un récipient comportant des disques de tamisage mutuellement espacés (2, 3) entre lesquels se trouve un empilage (5) essentiellement métallique sous la forme de nattes enroulées qui sont bobinées autour d'un noyau (4) du récipient, dans lequel de la sorte le récipient comporte au voisinage de chacune de ses extrémités un orifice d'entrée et un orifice de sortie, respectivement, pour le fluide de nettoyage.

2. Procédé selon la revendication 1, caractérisé en ce qu'on utilise des nattes de laine d'acier.

3. Procédé selon la revendication 1 ou la revendication 2, caractérisé en ce qu'on mesure le potentiel redox dans un filtrat du filtre réducteur (1) à l'intérieur du boitier contenant le filtre.

4. Filtre réducteur (1) pouvant être utilisé dans un procédé conforme à l'une quelconque des revendications précédentes, caractérisé en ce qu'il comprend essentiellement un récipient comportant des disques de tamisage (2, 3) mutuellement espacés entre lesquels se trouve un empilage (5) essentiellement métallique sous la forme de nattes enroulées qui sont bobinées autour d'un noyau (4) du récipient, lequel récipient est pourvu au voisinage de chacune de ses extrémités avec un orifice d'entrée et de sortie, respectivement, pour le fluide de nettoyage.

5. Filtre réducteur selon la revendication 4, caractérisé en ce qu'il constitue un dispositif pouvant être retiré.

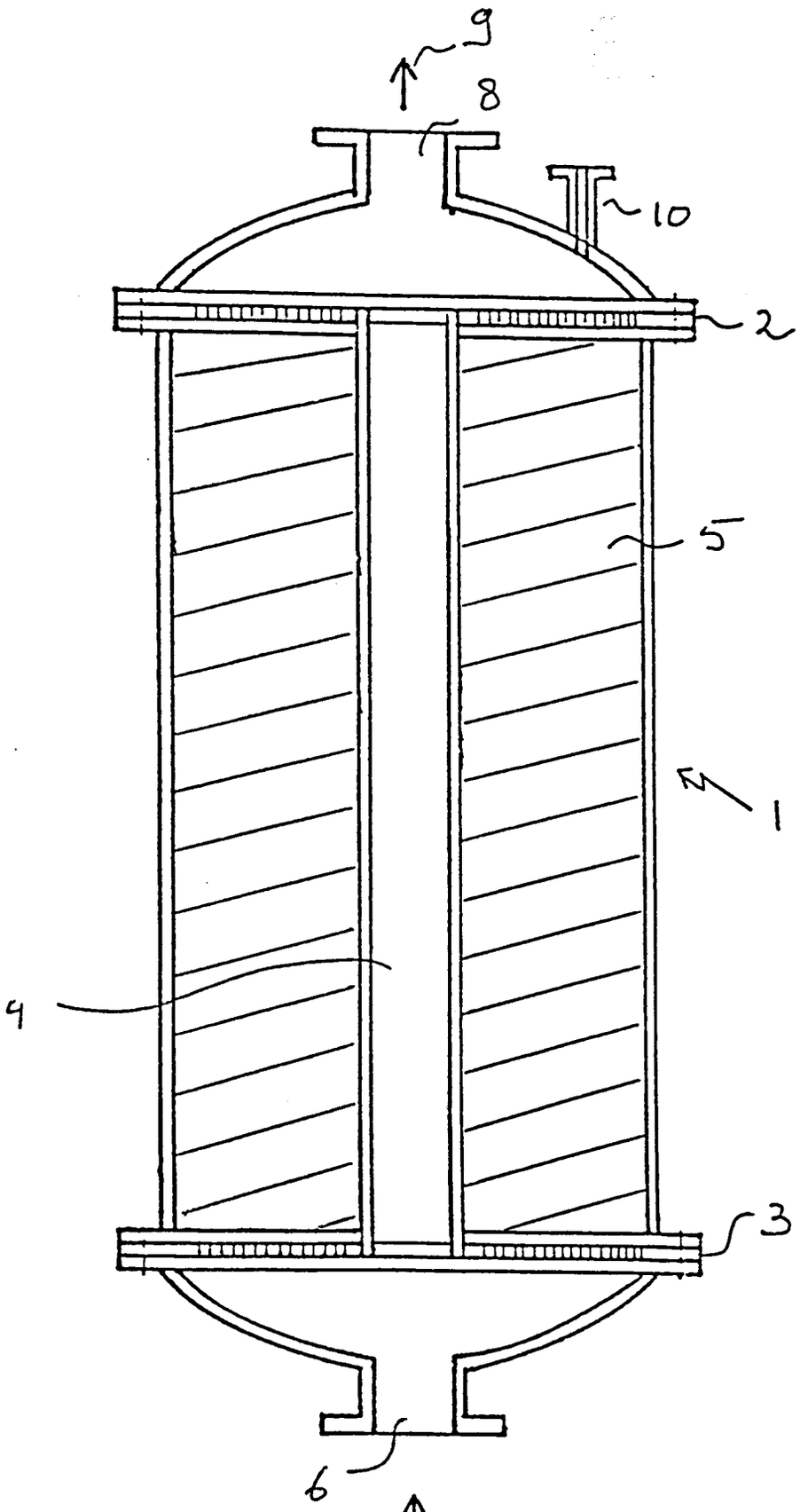


Fig 1

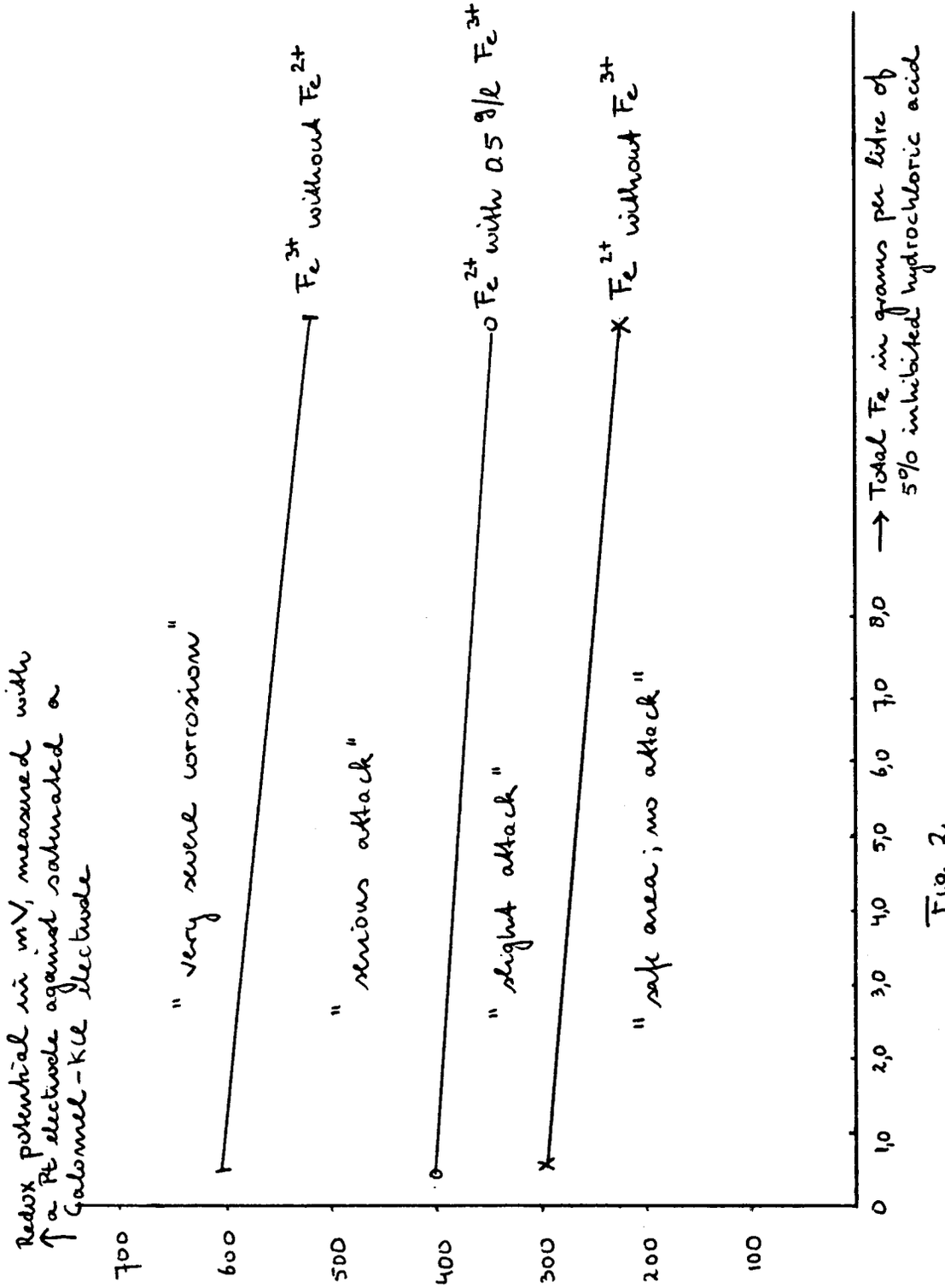

Redox potential in mV, measured with a Pt electrode against saturated a Calomel-Kle electrode
700
600
500
400
300
200
100
" very severe corrosion"
" serious attack"
" slight attack"
" safe area; no attack"
Fe^{3+} without Fe^{2+}
Fe^{2+} with 0.5 g/l Fe^{3+}
Fe^{2+} without Fe^{3+}
0
1,0
2,0
3,0
4,0
5,0
6,0
7,0
8,0
→ Total Fe in grams per litre of 5% inhibited hydrochloric acid

Fig. 2