

Dissolution of Iron Oxides

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Abstract : *This paper presents an in depth analysis of the DCB (dithionite-citrate-bicarbonate) method popularly adopted for iron oxide removal from clays as outlined by Mehra and Jackson (1960). We reviewed the reaction conditions of the DCB method and found several inconsistencies in the selection of procedures such as pH, method of washing, etc. We then carried out a theoretical analysis of the chemistry of dithionite reduction, deduced the effect of pH on the reduction potential and studied the fundamental mechanisms of iron dissolution. Analysis indicates that the basic arguments on which the DCB method is based, is not in agreement with theoretical facts. These flaws are discussed. To overcome the shortcomings of the DCB method, an alternative DCO (dithionite-carbonate-oxalate) method as proposed by Goswami et al. (1995) is briefly described here.*

Iron oxides in soils not only occur as discrete phases, but are also closely associated with silicate clays on the surfaces of which they may form coatings (Greenland and Hayes, 1978). By virtue of their ability to adhere to the surfaces of clay minerals, iron oxides may greatly modify their properties, particularly ion exchange behaviour and surface charge. The presence of iron oxides also complicates spectroscopic studies (XRD, IR, Mössbauer, etc.) of soil clays. Therefore, for the purpose of many investigations, the selective dissolution of iron oxides from the silicate clays, is an essential feature. Iron oxide removal procedures have been routinely adopted since several decades both for characterising silicate as well as for quantifying the influence of iron oxides on various chemical properties.

All the methods proposed till date, for selective dissolution of iron oxides, utilise reducing agents or complexants or a combination of the two. The notable earliest attempt was by Tamm (1922) who proposed the use of acid ammonium oxalate at pH 3.3. This method is popularly used even today, for evaluating amorphous iron oxides in soils; crystalline materials are, however, incompletely extracted by this method. The subsequent proposal of considerable importance appears to have been by Galabutskaya and Govorova (1934) who suggested the use of sodium dithionite at 40°C. This report left largely unrecognised by the rest of the world for about 16 years.

Taking a clue from the work of Galabutskaya and Govorova (1934), Deb (1950) tried to further explore the possibility of using dithionite (hydrosulphite) as a reducing agent. Studies on the dissolution of iron oxide from a soil clay at two different pH and temperatures using sodium dithionite in the presence of tartarate, showed that there was little difference in the amounts extracted due to higher pH or temperature. However, higher temperatures (60°C) caused the precipitation of ferrous sulphide (FeS). In another method, soil clay was treated with ammonium oxalate at pH 3.8 and placed in sunlight. Both the dithionite and oxalate-sunlight methods were found to dissolve goethite and hematite completely; amounts of Fe₂O₃ extracted from soil clays by these two methods were also similar. Tamm's solution (acid ammonium oxalate at pH 3.3), however, extracted much less Fe₂O₃. Of the two methods tried by Deb (1950), the dithionite method was reported to be less destructive towards clay minerals than the oxalate-sunlight method. However, even with dithionite, illite was not completely stable and montmorillonite containing iron was quite unstable.

Mitchell and Mackenzie (1954) considered that the addition of organic acids, in the method proposed by Deb (1950), made the subsequent analysis of the solutions rather tedious. To overcome this difficulty, they developed an essentially inorganic method. They concluded that treatment with sodium dithionite solution at 40°-45°C followed by 0.05 N HCl washing produced optimum results. Mackenzie (1954) subsequently modified the procedure by suggesting that sodium dithionite solution be used directly without any pH adjustment with NaOH.

Aguilera and Jackson (1953) considered that the reaction conditions prescribed by Deb (1950), viz., a pH of 5.4-6.0 and a temperature of 40°C, produced FeS and precipitation of S and was extremely slow in dissolving iron from Latosols. It may, however, be mentioned that according to Deb (1950), precipitation of FeS occurred only at 60°C and higher temperatures and the Fe₂O₃ in a deep red soil clay from *Nilgiri* (India) could be dissolved to the extent of 98-100%. The modification introduced by Aguilera and Jackson (1953), to overcome the difficulties they mentioned, included use of a citrate-versene solution at pH 7.3 and a temperature of 80° – 90°C. Although higher pH as well as higher temperatures favour the formation of FeS, this was not observed in their systems. The destructive effect on standard clays and soil clay minerals, as evidenced by reduction in CEC, was reported to be equivalent to that caused by other methods. Mehra and Jackson (1960) later introduced some more modifications on the previous technique by incorporating NaHCO₃ to maintain the pH at 7.3 and adding Na₂S₂O₄ in the solid form, instead of a solution. According to them, the dithionite-citrate system buffered with NaHCO₃ (DCB method) avoided precipitation of S and FeS and was also more efficient than all other previous methods. Of the various methods that have been recommended till-date, this DCB method is undoubtedly the most widely used. However, in spite of its popularity, there are far too many reports which show that it cannot be relied upon.

A. Efficiency of the dithionite-citrate-bicarbonate (DCB) method for the removal of iron oxides from soils and clays

There are numerous reports in the literature which provide convincing evidence for the fact that the DCB treatment does not always result in complete

dissolution of iron oxides. Borggaard (1982) observed that hematite was dissolved to the extent of only 50% after DCB treatment. Dissolution of goethite, hematite and even amorphous ferric oxide was also shown to be far from complete (Ryan and Gshwend, 1991); the Ti^{3+} -citrate-EDTA- NaHCO_3 method removed iron oxides more effectively and more selectively than the dithionite method. Shuman (1982) observed that the amounts of iron extracted from two Ultisols were low; whereas ascorbic acid-oxalate treatment could extract 100% and 67% of Fe from a Hapludult and a Rhodudult respectively, the corresponding figures for DCB extraction were 83% and 64.2%. Rueda *et al.* (1992) also reported that EDTA is a better complexant than citrate, for the dissolution of iron oxides by dithionite. Pawluk (1972) compared DCB extraction with acid-oxalate treatment and concluded that the latter removed more iron from both clay as well as silt fractions of a soil. Paglai and Sequi (1982) also concluded, from optical and chemical studies, that iron in nodules was more efficiently removed by acid ammonium oxalate rather than by DCB treatment. Extraction of Fe_2O_3 from four soils of Ghana was not complete by DCB treatment; photochemical oxalate treatment was more efficient in this regard (Endredy, 1963). Arocena *et al.* (1989) suggested, from studies with soil thin sections, that for complete iron oxide removal, the DCB extraction should be carried out for 1 h at 75°C.

By far the most convincing evidence, for the incompleteness of the DCB procedure for iron oxide removal, is provided by the Mössbauer studies as conducted by Ericsson *et al.* (1984). They showed that lepidocrocite and goethite, in a soil from northern Finland, could be removed after three DCB treatments. However, for an Oxisol (from Madeira, Spain) which contained goethite and hematite, one DCB treatment dissolved 36% of the total iron and three treatments resulted in only 43% of total iron being dissolved. The colour of the sample was red even after three DCB treatments and XRD analysis confirmed that hematite was present in the residue after three treatments. Mössbauer studies also showed that after one DCB treatment, the goethite was completely dissolved but the hematite was only partly affected. The same was observed after three DCB treatments. They stated that the DCB treatment was inefficient in removing hematite from the sample. This is surprising as Mehra and Jackson (1960) found their proposed method to be very efficient in dissolving crystalline hematite at the near neutral pH (7.3) maintained by the NaHCO_3 buffer.

B. An assessment of the arguments presented in developing the DCB proposal

Apart from the aforementioned criticism of the DCB treatment, other aspects of the proposal itself and various arguments on which the method is based, need to be reassessed. It may be mentioned here that the DCB method as proposed by Mehra and Jackson (1960) is actually a minor modification of an earlier proposal by Aguilera and Jackson (1953). Therefore, a scrutiny of the latter report is first necessary before the former can be assessed.

In the procedure recommended by Aguilera and Jackson (1953), the sample was mixed with a 0.3 M sodium citrate solution at pH 7.3 and placed on a water bath at 80°-90°C; to this was added a solution of sodium dithionite, adjusted to pH 7.3 by NaOH. The heating was continued for 15 min. Then saturated NaCl solution was added to the suspension, and centrifuged; Fe was estimated in the

supernatant. The residue was retreated, if necessary, and then washed with 80-99% methanol or 75% acetone. This sample was then considered ready for further analysis.

The two basic features of the method are, a reaction pH of 7.3 and a temperature of 80-90°C. The arguments presented by Aguilera and Jackson (1953) for the choice of that particular pH or temperature are self-contradictory. Thus, one of the reasons they initially stated for a reaction pH of 7.3 is that FeS does not precipitate at that pH; subsequently, they mentioned that in the presence of citrate (or oxalate) FeS does not precipitate “*even in a neutral or alkaline medium*”. Another reason for a pH of 7.3 is that “*the optimum sequestering action of versene is approximately at pH 7.0*”. However, in the proposed method, the addition of versene (EDTA) is considered optional, not essential. Therefore, it appears that any pH above 7.0 could have been chosen for the reaction and there is certainly nothing to recommend the particular pH of 7.3. This choice of pH is only based on some conflicting reasoning. The reasons for a reaction temperature of 80°-90°C, is also not clear and no experimental data or scientific logic has been advanced to justify it.

The recommended procedure itself has several stages which can cause serious errors. Aguilera and Jackson (1953) used a solution of sodium dithionite adjusted to pH 7.3; however, it is well-known that solutions of dithionite are unstable and undergo rapid self-decomposition (Bailar *et al.*, 1973). Therefore, the reducing agent used by them would not give consistent results unless particular precautions were taken to prepare a very fresh solution and use it immediately. No such precautions were mentioned by the authors.

For determining the amount of Fe dissolved after reaction, Aguilera and Jackson (1953) recommended adding saturated NaCl solution to the suspension, followed by centrifugation and decantation – for samples low in Fe (<5%), the reduction and centrifugation process was repeated once more; Fe was analysed in the two combined solutions. A serious objection to this procedure is that a single centrifugation each time, without any proper washing, cannot recover all the Fe that is adsorbed or occluded within the solid residue. In soils, a large amount of such residue will be present and consequently a significant amount of Fe would not have been recovered for analysis. Usually a minimum of five washings are necessary to quantitatively recover the dissolved solutes from a 1 g residue. For larger residues, more washings are necessary. Any data, which are based on a single centrifugation-decantation step after each reduction, cannot be considered to be particularly reliable.

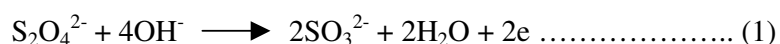
It is also recommended (Aguilera and Jackson, 1953) that the residue, after reduction and NaCl washing, be washed with methanol or acetone. The solubility of NaCl in methanol and acetone, is very low (about 0.2% and 0% respectively; NRC, 1928). In fact, the addition of these solutions to a concentrated NaCl solution causes NaCl to precipitate. Therefore, it is highly probable that the use of such solvents for washing the residue, may not result in complete removal of NaCl. The residue could, consequently, be contaminated with NaCl and also with other sodium salts like Na₂SO₃, Na₂S₂O₄, etc.

The method, adopted by Aguilera and Jackson (1953) for the analysis of Fe in the extracts, is also questionable. In order to remove interference by citrate and EDTA in Fe analysis, the authors used H₂O₂; at the end of H₂O₂ addition, the solution was yellow in colour. It has been observed by us that the oxidation of citric acid by H₂O₂ at 80°C is extremely slow and takes at least a week (Goswami, 1994). Within the time period suggested by the authors, citric acid cannot, thus, be completely oxidised. We also observed that EDTA is not oxidisable by H₂O₂. The presence of complexants even after H₂O₂ addition, in the solutions analysed by Aguilera and Jackson (1953), could further be confirmed by the fact that the solutions were yellow in colour but no precipitation of ferric hydroxide occurred. At any pH > 3, Fe³⁺ will precipitate as the hydroxide (Cotton and Wilkinson, 1969) unless complexants are present to keep it in the solution. The presence of such complexants may, however, cause errors in the subsequent analysis of Fe.

Examination of the published X-ray diffractograms of soil samples (Aguilera and Jackson, 1953), before and after treatment for removal of Fe₂O₃, also indicates several anomalies. Thus, the diffractogram of an aluminous Latosol (Haiti) shows a distinct line at 2.69 Å (due to hematite) not only in the original sample but also in the treated sample; its intensity is only slightly reduced in the latter and the presence of hematite is definitely indicated. Another soil (Wahaiwa Latosol from Hawaii) supposedly contains 15-20% iron oxide but peaks due to iron oxides are not evident from the diffractograms presented by them. In fact, the authors claim that the soil contains "18% crystalline hematite" which is "completely removed by the procedure in 15 min." There is no evidence in the XRD data presented by the authors, to substantiate their claim.

From the various discrepancies of the Aguilera and Jackson (1953) report, it appears that their proposed method is not based on very sound experimental and logical evidence. The DCB method, as it is used today, has its roots in the former proposal of Aguilera and Jackson (1953). Indeed, the reaction conditions in the DCB method, are all the same as in the previous method, the differences being that the pH of 7.3 is maintained using a NaHCO₃ buffer and dithionite is added as a solid, instead of a solution. Here, various arguments have been advanced to justify the selection of a reaction pH of 7.3, although it was seen previously that the choice of this particular pH was quite arbitrary and without any chemical basis. Washing and analytical techniques recommended are also almost the same as in the previous report. The various logical and experimental shortcomings of the report by Mehra and Jackson (1960) will also be analysed here in detail.

The variation in the oxidation potential of dithionite with pH was presented by Mehra and Jackson (1960) in their article. However, there was no mention of how these values were obtained, i.e., by experimental means or by theoretical calculations. The standard oxidation potential (E⁰) of dithionite is 1.12 V (Weast, 1985-1986). According to the reaction (Cotton and Wilkinson, 1969),



the redox potential is highly dependent on the OH⁻ concentration (i.e., pH) of the solution. The dependence is given by the relation (Glasstone, 1972),

$$E = E^0 - (RT/nF) \ln ([\text{SO}_3]^{2-} / [\text{S}_2\text{O}_4]^{2-} \cdot [\text{OH}]^4) \dots\dots\dots (2)$$

When the activities of the reactants and products are all equal to one, i.e., at 1 N (dithionite and sulphite concentration of 1 N and at pH 14), the oxidation potential of the system would be equal to its standard value, i.e., $E = E^\circ$. Mehra and Jackson (1960) mentioned that their systems failed to attain the standard value of 1.12 V; this is expected, since none of the aforesaid required conditions were fulfilled in their systems. The authors also mentioned that the use of NaHCO_3 instead of NaOH , gave a “*well regulated, high oxidation potential of 0.7 V.*” This observation is not compatible with the chemistry of dithionite oxidation because (i) oxidation potential of dithionite is solely dependent on the pH of the solution irrespective of the nature of the alkali (whether NaOH or NaHCO_3 or any other) and (ii) the oxidation potential of the solution will reduce rapidly (Wayman and Lem, 1970) with time since the dithionite ion ($\text{S}_2\text{O}_4^{2-}$) is converted to sulphite (SO_3^{2-}) thereby lowering the value of E , as seen in eqn. (2). Therefore, it is not possible, for a solution containing dithionite, to have an almost constant oxidation potential, as reported by Mehra and Jackson (1960) for the NaHCO_3 system.

Information on the “*solubility of Fe_2O_3 with different procedures and pH levels*” also does not confirm to chemical logic and is self-contradictory. According to Mehra and Jackson (1960), the precipitation of FeS occurred between pH 6.30 and 6.40 and also at pH 7.20 but not at pH 6.80 to 12.16. However, according to the previous observations of Aguilera and Jackson (1953), the precipitation of FeS did not occur in the presence of citrate in a neutral or alkaline pH. These two reports are, therefore, contradictory. Moreover, FeS is stable at higher pH and dissolves in acidic solutions; therefore, the formation of FeS , if any, should be more prominent in procedures employed at highly alkaline solution (pH > 12) rather than in the solutions with pH < 7. It may be mentioned here that Aguilera and Jackson (1953) did not observe the formation of FeS in their systems (pH 7.3) whereas Mehra and Jackson (1960) reported the formation of FeS in a similar system.

Mehra and Jackson (1960) have subsequently attempted to justify the choice of a reaction pH of 7.3, based on the intersection of the oxidation potential curve for dithionite with the solubility curve of Fe_2O_3 . According to the authors, the “*oxidation potential increases sharply up to pH 8 and then levels off.*” It is not known how the authors came to this conclusion because according to the reaction mechanism, the value of the oxidation potential (E) increases linearly with increase in OH^- concentration (eqn. 1); it reaches a value of 1.12 V under standard conditions (as mentioned earlier). Hence the observation by Mehra and Jackson (1960) that the oxidation potential levels off at about 0.7 V at a pH 8.0 and above, is difficult to rationalise.

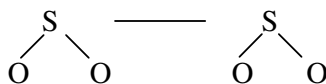
The solubility of Fe_2O_3 with two procedures carried out by Mehra and Jackson (1960) do not match at all. Thus, by utilising one procedure, the solubility of Fe_2O_3 at pH 7.4 is only 65.1%; while with another procedure, it is reported that 100% dissolution can be obtained at about the same pH. Normally, solubility *versus* pH studies should have been done independent of procedures employed; this has not been done. Therefore, both the set of data, viz., oxidation potential and solubility, on which the choice of pH 7.3 has been justified, are doubtful.

The procedure enumerated by Mehra and Jackson (1960) for washing the treated residue to recover soluble ions, is the same as that proposed earlier by Aguilera and Jackson (1953) and, therefore, suffers from the same drawbacks as mentioned previously. Briefly, the number of washings are too few and the addition of acetone can cause precipitation of NaCl in the residue. The analytical method adopted for the determination of Fe is also the same as that used by Aguilera and Jackson (1953) and, hence, is subject to the same sources of error as outlined earlier. It is regrettable that no XRD data of soils before and after DCB treatment are provided. This might have served to confirm that removal of iron oxides from soils is fairly complete. From the results provided by Mehra and Jackson (1960), thus, there is no way of judging whether complete extraction has indeed occurred.

After a detailed scrutiny of the DCB proposal from its roots, viz., the works of Aguilera and Jackson (1953) and Mehra and Jackson (1960), it appears that there are far too many sources of error and questionable arguments. In short, these are (i) incomplete dissolution of iron oxides, as reported by many, (ii) an arbitrary choice of pH at 7.3 with rather loose arguments to justify it at a later stage, (iii) no particular reasons for fixing the reaction temperature at 80°C, (iv) efficiency of recommended washing procedure doubtful, (v) method adopted for analysis of Fe subject to error, and (vi) insufficient conclusive evidence for complete removal of iron oxides from soils/clays. As a consequence of these various sources of error, it is possible that the reaction is not being carried out under conditions of maximum efficiency. In order to obtain a more reliable method, the reaction must be studied anew, from its very fundamentals.

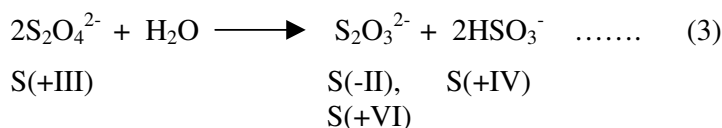
C. Mechanism of reduction by sodium dithionite

In sodium dithionite, Na₂S₂O₄, sulphur is in the oxidation state of +3. This is the lowest possible oxidation number that S can assume in its oxyacids or derivatives thereof (Bailar *et al.*, 1973). In earlier literature, there appeared to be some controversy regarding the structure of the dithionite ion, S₂O₄²⁻, but this has now been resolved by X-ray crystallographic studies. The shape of the ion is,

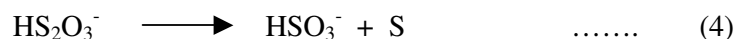


with a rather long S-S bond length of 2.389 Å. The SO₂ planes are almost parallel and elipsed. This unusual and unstable configuration of the molecule explains why the S₂O₄²⁻ ion is unstable in solution (Brasted, 1961; Bailar *et al.*, 1973).

Dithionites are stable as dry solids but decompose in aqueous solutions by disproportionation according to the equation (Bailar *et al.*, 1973),

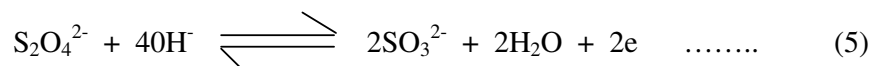


In acid solutions, such hydrolysis is more rapid and follows second order kinetics. Elemental sulphur is also produced, probably due to the decomposition of the thiosulphate, $S_2O_3^{2-}$ ion (Moellar, 1973) as,



This reaction occurs at proton concentrations in excess of 10^{-5} M (i.e., pH < 5.0). On the other hand, in neutral and alkaline media, the thiosulphate ion is perfectly stable (Moellar, 1973). Therefore, reactions of dithionite carried out in neutral or alkaline media will not cause deposition of sulphur. This aspect of the reaction does not appear to have been considered by previous workers (Deb, 1950; Mitchell and Mackenzie, 1954; Mehra and Jackson, 1960).

Dithionites are strong reducing agents in alkaline solutions where the following reaction occurs (Cotton and Wilkinson, 1969),



which has a standard oxidation potential, $E^\circ = 1.12$ V. On the other hand, in acid solution, the reaction occurs as,



which has a E° of 0.056 V (Weast, 1985-86). Therefore, dithionites are stronger reducing agents in alkaline than in acid solutions.

Here, the oxidation potentials (E) for dithionite solutions at different pH, from 6.0 to 14.0, were calculated using the Nernst equation (Glasstone, 1972). Briefly, the procedure is as follows :

For any redox reaction, the redox potential, E, is related to the standard potential, E° , as,

$$E = E^\circ - (RT/nF) \ln (a_p/a_r) \quad \dots\dots (7)$$

where R is the gas constant, T the temperature in degree Kelvin, n the number of electrons, F the Faraday constant, and a_p and a_r refer to the activities of products and reactants, respectively. For the reaction (5), this gives,

$$E = E^\circ - (RT/2F) \ln ([SO_3^{2-}]^2 / [S_2O_4^{2-}]^2 \cdot [OH^-]^4) \quad \dots\dots (8)$$

or

$$E = E^\circ - (RT/2F) \ln ([SO_3^{2-}]^2 / [S_2O_4^{2-}]^2) + (RT/2F) \ln [OH^-]^4 \quad \dots\dots (9)$$

when activities of SO_3^{2-} and $S_2O_4^{2-}$ are both equal to 1, the eqn. (9) reduces to,

$$E = E^\circ + (RT/2F) \ln [OH^-]^4 \quad \dots\dots (10)$$

By using the relation,

$$[\text{H}] \cdot [\text{OH}] = 10^{-14} \quad \dots\dots (11)$$

We have,

$$E = E^{\circ} + (4RT/2F) \ln (10^{-14} / [\text{H}]) \quad \dots\dots(12)$$

or
$$E = E^{\circ} + (4RT/2F) \ln 10^{-14} - (4RT/2F) \ln [\text{H}] \quad \dots\dots (13)$$

or
$$E = E^{\circ} + (4RT/2F) \ln 10^{-14} + 2.303 (4RT/2F) \text{pH} \quad \dots\dots (14)$$

At 25°C, or 298°K, the eqn. (14) reduces to,

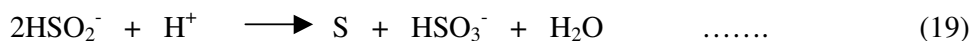
$$E = E^{\circ} - 1.652 + 0.118 \text{ pH} \quad \dots\dots (15)$$

The values of oxidation potential E, for the reaction (5), are thereby obtained and are as follows :

<i>pH</i>	6.0	7.0	8.0	9.0	10.0	11.0	12.0	13.0	14.0
<i>E (in V)</i>	0.176	0.294	0.412	0.530	0.648	0.766	0.884	1.002	1.120

Thus, the standard oxidation potential value of 1.12 V is reached at pH 14; below this pH, the values of E are lower. Thus, the reducing power of dithionite increases rapidly with pH, and any reduction reaction using dithionite should logically be more efficient at alkaline pH, in contrast to the conditions used by Deb (1950) and Mitchell and Mackenzie (1954) where the reaction pH was 7.0.

The mechanism of decomposition of aqueous dithionite was studied by Wayman and Lem (1970). According to them, decomposition begins with a slow induction period followed by a rapid phase (*using dithionite solutions for iron oxide dissolution is, therefore, disadvantageous*). Although the overall reaction is as described in eqn. (3), side reactions may occur with the formation of H₂S and S. The sequence of reactions leading to the latter products, occur by the following route (Wayman and Lem, 1970) :



The sulphyxylate ion, HSO₂⁻, is produced as an intermediate (eqn. 16); this may react with dithionite to form thiosulphate (eqn. 17) or with H⁺ to form H₂S or S (eqn. 18, 19). Such side reactions can account for the formation of sulphides (FeS) observed during the reduction of iron oxides by dithionite (Deb, 1950; Mehra and Jackson, 1960). According to Wayman and Lem (1970), the H₂S as well S, which are produced, have a catalytic action on the reaction (eqn. 17) and may themselves

be consumed in the process. Thus H_2S may react with sulphoxylate, HSO_2^- , to form S.



Wayman and Lem (1970) also pointed out that the white milky cloud of S which is formed in the initial phase of dithionite decomposition, is subsequently dissolved over a period of time. Thus, it would appear that in dithionite solutions, of slightly acidic to alkaline pH, both H_2S as well as S would only be transient phases. The persistence of FeS during iron oxide dissolution by dithionite can, therefore, be due to the fact that H_2S reacts with Fe^{2+} forming FeS, which being insoluble, is no longer available for further reaction (as in eqn. 20). Unless some chemical agents are present in the system, which can dissolve the FeS (e.g., strong Fe^{2+} complexants), the accumulation of FeS is inevitable. Thus, a knowledge of the chemistry of dithionite can itself provide some of the prerequisites for efficient dissolution.

D. Fundamentals of iron oxide dissolution

The solubility of metal oxides of the M(III) and M(IV) species in aqueous systems is very low; generally moderate to high mineral acid concentrations are required to achieve dissolution of such metal oxides. However, in some instances, as with iron oxides, dissolution can take place through changes in oxidation state of the metal. In these cases, solubility is a function of solution potential (Blesa and Maroto, 1986). Thermodynamically, this may be represented as



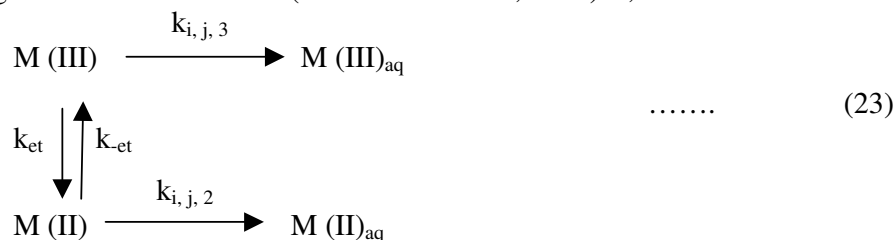
A further way to enhance solubility is the use of complexing agents which lower the activity of M (II) in the aqueous phase.

A general case of dissolution of solids may be represented by three stages, any of which may be rate-limiting. These stages are, (i) the diffusion of a kink unit of a crystal to a layer edge, (ii) diffusion from layer edge to the plane surface, and finally, (iii) diffusion from the plane surface to the bulk of the solution (Dibble and Tiller, 1981). Following the general theories of solid state reactivity, Valverde and Wagner (1976) derived an expression for the dissolution of oxides involving reduction as well as complexation. Here, specific reaction rate, R, is expressed as a sum of the rates of dissolution of both oxidized and reduced states of M, i.e., M(III) and M(II), as given by

$$\begin{aligned} r = & \sum_i \sum_j k_{i,j,2} \Gamma_{i,j,2} \exp(\alpha_{i,j,2} z_{i,j,2} F \Delta\Psi / RT) \\ & + \sum_i \sum_j k_{i,j,3} \Gamma_{i,j,3} \exp(\alpha_{i,j,3} z_{i,j,3} F \Delta\Psi / RT) \quad \dots\dots \\ (22) \end{aligned}$$

Here, i is the number of ligands bound to kinks, j the number of H^+ ions associated with surface O, $\Gamma_{i,j}$ surface densities of such kinks, $k_{i,j}$ their specific rate constants, $\Delta\Psi$ the potential difference of the ions between the surface and solution, α the electrochemical transfer coefficient, z the valency, and F , R and T the Faraday constant, gas constant and absolute temperature, respectively.

The eqn. (22), however, does not take into account, the possibility that the charge transfer process itself [i.e., $M(III) \longrightarrow M(II)$] may be rate-limiting. A more general kinetics scheme (Blesa and Maroto, 1986) is,



Thus, k_{et} (rate constant) may also control the rate process. Studies on dissolution of iron oxides (Gorichev and Kipriyanov, 1984) have shown that any one of the k values in eqn. (23) may be rate-limiting depending on the experimental conditions.

Investigating the reductions of metal complexes by dithionite, Balahura and Johnson (1987) represented the reduction reaction in the following manner :



Thus, the dominant reducing agent is the SO_2^- radical which results from the dissolution of $S_2O_4^{2-}$. The SO_2^- is an effective reducing agent for a wide variety of complexes and reacts by simple outer-sphere electron transfer (Balahura and Johnson, 1987).

The photoreductive dissolution of lepidocrocite (γ -FeOOH) in the presence of citrate was studied by Waite and Morel (1984). According to their dissolution model, citrate ion is first adsorbed at the surface of lepidocrocite; the Fe^{3+} -citrate complex at the surface is then reduced by light to a surface bound Fe^{2+} -citrate complex. Subsequently, the Fe^{2+} -citrate is removed into the solution phase. At the first stage, the formation of the surface complex is initially extremely rapid in the presence of excess adsorbate. The dissolution rate is proportional to the concentration of adsorbed citrate. Once the reduced Fe^{2+} -citrate species are formed, they rapidly leave the γ -FeOOH surface, i.e., there is no significant build up of Fe^{2+} at the surface.

From the studies on the reactions of dithionite and the dissolution of iron oxides available in the literature, the following general inferences may be drawn : In reductions using dithionite, an alkaline pH is to be preferred since the reducing power of dithionite is low in the acidic range and increases with increase in pH; moreover, the precipitation of elemental S is also avoided thereby. Since

dithionites produce H_2S in side reactions, FeS will inevitably form when iron oxides are reduced by dithionite; the formation of FeS can be avoided by using efficient Fe^{2+} -complexants whereupon H_2S is consumed by further reaction. When a complexant is present, the first stage of reaction is the adsorption of the complexant on the surface of iron oxide. The Fe^{3+} -complex is then reduced by the SO_2^- radical generated by the fission of a dithionite ion; this is an outer-sphere electron transfer process. The Fe^{2+} -complex which is still surface bound then rapidly leaves the surface and goes into solution as the Fe(II) complex. Since this last stage is very rapid, the reaction rate would probably be controlled by the stages (i) $\text{surface-Fe}^{3+} + \text{complex} \rightarrow \text{surface-Fe}^{3+} \text{ complex}$, and (ii) $\text{surface-Fe}^{3+} \text{ complex} + \text{reductant} \rightarrow \text{surface-Fe}^{2+} \text{ complex}$. Other factors which would also greatly influence dissolution, according to the Valverde and Wagner (1976) model as shown in eqn. (22), are, (i) the crystal structure, particularly defect regions which influence the concentration of kinks, (ii) deviation from ideal stoichiometric composition of the oxide, (iii) substitution of ions in the crystal, (iv) surface area, (v) stability of the Fe^{2+} and Fe^{3+} -complexes, and (vi) temperature of reaction.

E. Development of a new method (Goswami, 1994)

Initially, an experimental survey was done using natural goethite, to obtain some idea of the relative efficiencies of various reagents in dissolving iron oxide. Dilute acids, sodium sulphite in acid and alkaline media, and Mg -powder in dilute acids, proved ineffective in dissolving goethite. Sodium dithionite in dilute HCl produced little change, but in dilute NaOH , a green precipitate was obtained. This precipitate was completely soluble in oxalic acid but only partially soluble in EDTA , DTPA , salicylic and citric acids. These experiments suggest that sodium dithionite should be used in an alkaline solution. Ferrous hydroxide is produced on such reduction and, therefore, complexants are necessary to dissolve Fe^{2+} ; oxalic acid appears to be the most efficient in this regard.

Experiments were subsequently done, to obtain the most efficient reaction conditions for the dissolution of iron oxides. The effect of (i) complexant, (ii) temperature, (iii) pH , (iv) amount of complexant, (v) period of reaction, (vi) quantity of dithionite and its mode of addition were studied.

Regarding complexant effect, it was interesting to note that citrate was much less efficient than oxalate; dissolution roughly followed the order, salicylate < EDTA < citrate < oxalate. The influence of temperature was not very pronounced with the synthetic mineral which showed more than 90% dissolution at room temperature. However, higher temperatures were necessary for dissolving natural minerals; maximum dissolution was possible only at 100°C .

Variations in the amount of sodium carbonate were done to induce changes in the pH of the solutions. Dissolution increased with an increase in pH up to 8.05, after which it decreased again. At acidic pH , the precipitation of sulphur occurred. Lower dissolution at very high pH was probably due the competitive effect of OH^- ions over $(\text{COO})^{2-}$ ions for the Fe^{2+} . Studies on the effect of volume of oxalate reagent also showed that dissolution increased with increasing volume of oxalate, reached a maximum and then decreased again at

higher volumes of oxalate. This was attributed to the lowering of pH of the solution which occurred on addition of sodium dithionite. Apparently, a slight reduction in pH (to about 6) is favourable for Fe^{2+} dissolution but with excess oxalate, the solution is well-buffered and the pH is not reduced sufficiently. A solution volume of 30 mL was found to be the optimum for every 2 g of sodium dithionite.

Studies on iron oxide dissolution at various time intervals showed that maximum amounts were dissolved at 30 min. Lowering of dissolved iron level on prolonged heating might be caused by reprecipitation reactions. Dissolution also showed a high dependence on the amount of dithionite added. Under the reaction conditions, 2 g sodium dithionite is the optimum. Small amounts cause incomplete dissolution and with an excess of it, the solution becomes too acidic thereby reducing reaction rates. Moreover, the mode of addition of dithionite was also observed to significantly influence iron oxide dissolution. Addition in split doses was found to be more effective than addition in a single dose. This may be due to better contact between the reducing agent (which is very rapidly decomposed) and the mineral, when the former is added in small doses rather at one time.

From these aforementioned studies, it was possible to obtain the optimum conditions for iron oxide dissolution. This combination of parameters provides a dissolution efficiency of almost 100% for the synthetic and natural iron oxides studied. These reaction conditions are, however, closely inter-linked so that if one factor is altered, several others would have to be altered. Therefore, it is important that the reaction conditions be strictly adhered to, without attempting to change even one of them.

F. The dithionite-carbonate-oxalate (DCO) method (Goswami et al., 1995)

The amount of sample to be taken for the treatment, depends on the amount of Fe_2O_3 it contains; the reagents quantified here, are for samples containing no more than 50 mg Fe_2O_3 . Thus, 1 g of a soil clay containing 5% Fe_2O_3 may be taken in one set; if 5 g of such clay is required to be treated, then 5 such sets may be prepared. All clays have to be converted to the Na^+ or K^+ form prior to reaction, by washing with excess 1 N NaCl or KCl solution. This is essential because the presence of exchangeable Ca^{2+} (or similar ions) can cause the precipitation of insoluble oxalate, dithionite or sulphate.

Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (33.3 g) and anhydrous sodium carbonate, Na_2CO_3 (35.3 g) are weighed into a 1 L volumetric flask, dissolved in water with slight heating (whereupon oxalic acid is converted to sodium oxalate), cooled and made to volume. The pH of this solution is 8.05. In a 250 mL conical flask, 30 mL of the oxalate solution is taken and a weighed amount of sample is added to it (about 0.05 g iron oxide, 0.1 g Oxisol clay, 0.4 g Ultisol clay, 0.5 g Alfisol clay or 10 g standard clay mineral). It is important to ensure that the solution depth should be no more than about 1.5 cm; since reduction of dithionite occurs instantaneously within a few cm of the surface of the solution, in solutions of greater depth, the mineral tends to remain at the bottom of the flask and contact with the reducing zone is incomplete. Hence, a 250 mL conical flask is recommended for 30 mL solution. If a slightly larger amount of Fe_2O_3 (> 50 mg) is to be dissolved, the

required amount of oxalate solution will be proportionately higher and, therefore, the reaction may be carried out in a larger flask ensuring a shallow solution depth.

The suspension is placed in a boiling (distilled) water bath and its temperature is recorded. When the temperature reaches $100^{\circ}\text{C} (\pm 2^{\circ})$, 0.4 g sodium dithionite, $\text{Na}_2\text{S}_2\text{O}_4$, is added with continuous and vigorous stirring of the solution. This process is repeated every 5 min till a total of 2 g $\text{Na}_2\text{S}_2\text{O}_4$ is added; 30 min after the first addition (i.e., 10 min after the last addition), the flask is removed and cooled to room temperature. (It is important to note here that the sodium dithionite reagent should be stored in a desiccator since at room humidity, it readily absorbs moisture causing decomposition and loss of efficiency). The reacted suspension is centrifuged and the supernatant collected in a volumetric flask (if necessary). Further washing is done with 1N KCl (or NaCl) solution to prevent dispersion of clay. This is continued till the washings are free of $(\text{COO})^{2-}$ and $\text{S}_2\text{O}_4^{2-}$ (no decolorisation of dilute KMnO_4 solution in 0.1 N H_2SO_4) and also SO_4^{2-} and SO_3^{2-} (no white precipitate with BaCl_2 solution). At least 5 washings are required, in general. Washings are continued at least twice more after the tests are negative, and all washings (including the supernatant prior to 1N KCl/ NaCl wash) are collected for analysis. After this stage, the clays may be converted to the Ca^{2+} or any other ionic form as required. Incomplete washing may cause the precipitation of calcium oxalate, dithionite, sulphite or sulphate. The summarised method is given in a Flow sheet.

It has been observed by us, that soil clays treated with H_2O_2 for organic matter removal, sometimes show considerable amounts of $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in their XRD patterns. This is particularly evident in soils rich in organic matter (Saikh, 1994). Here, apparently the reaction of H_2O_2 with organic matter produces oxalate which then reacts with the Ca^{2+} in the soil to precipitate calcium oxalate. Therefore, it is desirable that the clay or soil be converted to the Na^+ or K^+ form prior to H_2O_2 treatment itself. However, if due to some mistake, calcium oxalate artifacts are observed to have formed, the only way they can be removed is by treatment with 1N HCl for a few minutes followed by centrifugation and washing. This drastic treatment is, however, unnecessary if the aforementioned precautions are taken.

Experiments to assess the effect of DCO-treatment were subsequently done (Goswami et al., 1995). The samples, taken for this, included standard clay minerals, soil clays and the iron oxide minerals. For comparative analysis, the same minerals were also treated by the DCB method of Mehra and Jackson (1960).

Data for Fe dissolution showed that with every mineral studied, the DCO method proposed here, resulted in greater dissolution compared to the DCB method of Mehra and Jackson (1960). Thus, the respective figures for Fe dissolved by DCO treatment and DCB treatment were respectively, > 99% and 90% for goethites, 97.73% and 79.67% for natural hematite, 100% and 65.15% for Oxisol clay, and > 95% and around 70% for Ultisol and Alfisol clays. Even with standard clay minerals, the amounts of Fe dissolved by DCO method were more than the DCB treatment.

Data on Al dissolution, however, showed that less Al was removed from standard clay minerals by DCO treatment than by DCB treatment. On the other hand, soil clays (which contain Al-substitution in their iron oxides) showed larger amounts of Al dissolution by the DCO treatment. It may be inferred that whereas iron oxides are more efficiently dissolved by the DCO treatment, dissolution of the silicate clay minerals are less than that by the DCB method indicating DCO to be safer method. Data on Si dissolution showed mixed trends which is probably due to the variable amounts of silica impurities in many of the samples.

Overall the chemical data suggest that the DCO treatment is highly selective for iron oxides. Whereas iron oxides were almost completely (>99%) dissolved by this method, its effect on the structural components of clay minerals was insignificant. However, for further confirmation of the effect of DCO treatment, CEC, XRD and DTA studies were also done (Goswami *et al.*, 1995).

Cation exchange capacity (CEC) data indicated that DCO treatment resulted in significant increases in CEC of kaolinite, illite and montmorillonite. This is in contrast to the results obtained by previous workers. It further proved that significant structural damage to the clay minerals did not occur. CEC of soil clays also increased greatly after the DCO treatment. Such increases may be attributed to the cleaning of the clay surface and exposure of the exchange sites which were previously densely coated with iron oxides.

Differential thermal analysis (DTA) of standard clay minerals, before and after DCO treatment, showed practically no change in the positions of the endotherms. Soil clays showed unmasking of the kaolinite endotherms as a result DCO treatment.

X-ray diffraction analysis (XRD) provided interesting results on the positive impact of DCO treatment. All the three standard clay minerals showed improvements in their XRD patterns. In general, basal reflections were sharpened while amorphous bands were reduced in intensity. Soil clays showed the most remarkable improvements. In Alfisol clay, after DCO treatment, the reflections of kaolinite and illite were much more prominent. The 7.25 , 4.48 , 4.27 and 3.53×10^{-1} nm lines due to the kaolinite were more sharp and the 3.35 line of illite increased greatly in intensity. Increased intensity and sharpness of kaolinite reflections were also observed in DCO-treated Ultisol clay. Oxisol clay showed even more prominent changes. Whereas the untreated clay showed only a single broad reflection of kaolinite (7.3×10^{-1} nm), all the major reflections could be observed as sharp lines after DCO treatment; gibbsite could also be detected. Reflections due to iron oxides, which were present in untreated soil clays, were no longer detectable after DCO treatment.

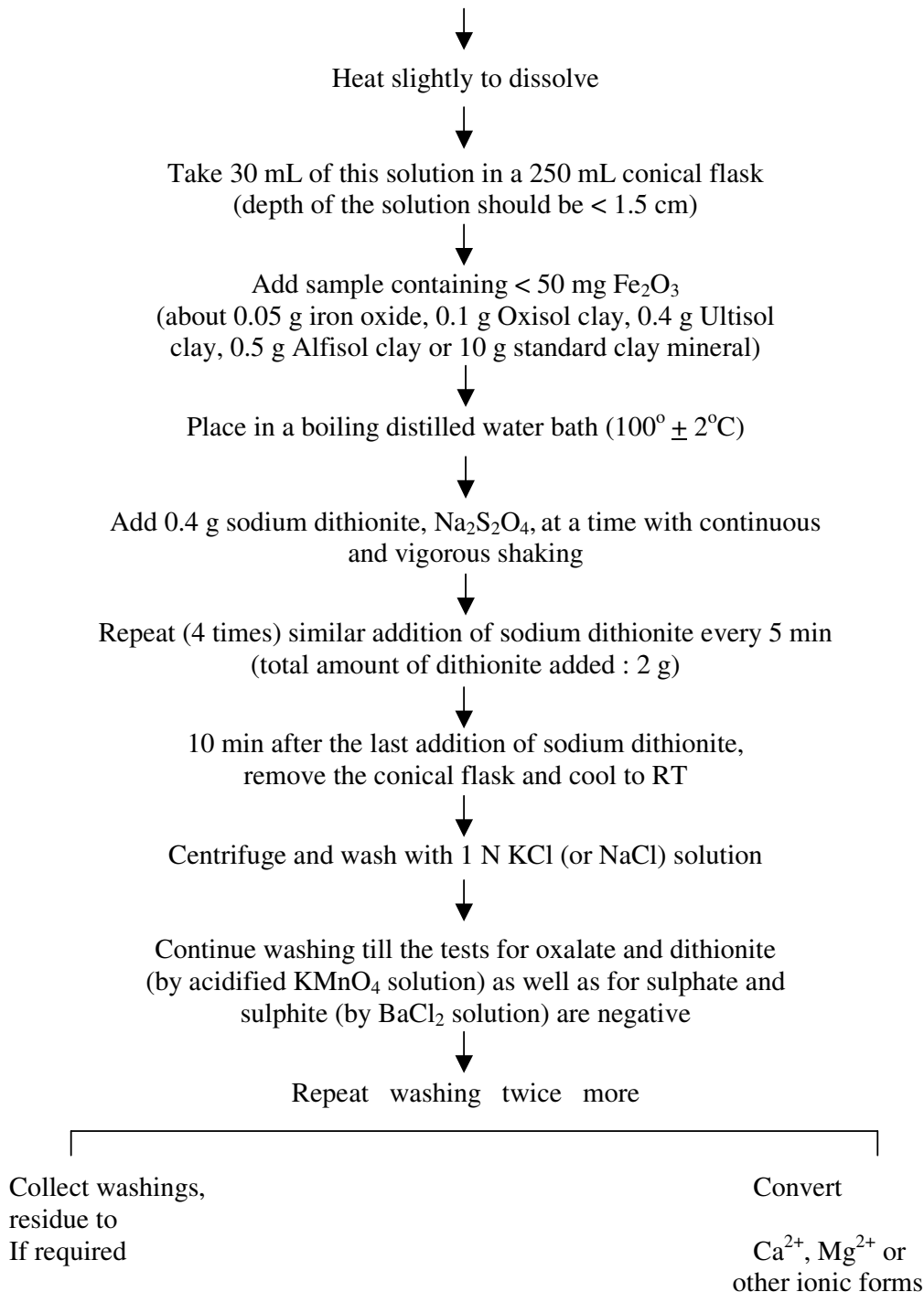
It was concluded that (i) the DCO method is superior to the DCB method, (ii) the DCO treatment causes no significant solubilisation of silicate clay structural cations, (iii) it results in an increase in the CEC of clays, (iv) thermal changes are more readily detectable in treated soil clays and (v) XRD patterns are improved.

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Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (33.3 g/L) + Sodium Carbonate, Na_2CO_3 (35.3 g/L)



[Note : Prior to organic matter removal by H_2O_2 , clay or soil sample is to be converted to K^+ or Na^+ form.]

Fig. 1 : Flow chart for removal of iron oxide