Could not this cation exchange capacity origiaate from a small amount of aluminium as impurity?

Dr K. Jasmund.—During the last war, Prof. Correns made similar experiments in synthesis at temperatures of 20° and 80°C. The apparatus used was similar to that of Hénin. Only a few characteristic lines appeared on the X-ray photographs, indicating that clay minerals were in the crystalline state. Perhaps the concentration was too small to allow the formation of sufficiently large crystals in sufficient quantity.

Mr R. H. S. Robertson.—High cation exchange capacity is no criterion of crystallinity in mixed oxide gels, *e.g.*, in Al_2O_3-SiO_2 gel catalysts. The uncrystallized coprecipitated mixed gels often have high exchange capacity, because Al, Mg, etc., proxy for Si in Si-O-Si-O networks in 4-co-ordination. The reactants in this case are, of course, concentrated. (See C. L. Thomas, Chemistry of Cracking Catalysts, *Ind. Engng. Chem.*, (1949), **41**, 2564-2573).

Dr R. Greene-Kelly.—In reply to this suggestion that industrial magnesium-silica gels have high exchange capacities due to replacement of silicon atoms in 4–co-ordination by magnesium, I think it is more likely that the exchange capacity arises from accidental impurities, than from isomorphous replacement between two atoms of widely differing size.

THE REMOVAL OF FREE IRON OXIDE FROM CLAYS*

BY B. D. MITCHELL and R. C. MACKENZIE.

Read 10th April. 1953.

The techniques previously employed in this laboratory for removing free iron oxide† from soil clays were the acid ammonium oxalate and the aluminium-ammonium tartrate methods (Tamm, 1922; Dion, 1944). Since both had disadvantages, especially when determining the iron by sodium salicylate (Scott, 1941), the use of sodium hydrosulphite, $Na_2S_2O_4$, (Galabutskaya and Govorova, 1934; Deb, 1950) was fully investigated in the hope that it might lead to the development of a satisfactory, completely inorganic procedure.

Method.—The thoroughly-wetted clay (20-40 mg.) is treated with a *fresh* 4 per cent. solution of sodium hydrosulphite of pH 5·8-6·0 (adjusted by sodium hydroxide solution) at 40-45°C for 15 minutes, the suspension centrifuged, and the supernatant liquid collected. The clay is then treated with 0·05 N hydrochloric acid at 40°C for 3 minutes, recentrifuged, and the supernatant liquid collected in a separate beaker. This complete treatment is repeated, and the clay is finally washed twice with neutral N sodium chloride solution.

*This is a brief summary. For full details consult the papers of Mitchell and Mackenzie (1954) and Mackenzie (1954).

†The term "free iron oxide" includes all iron not present in the crystal lattice of any component mineral, excepting of course the iron oxide minerals themselves.

The extracts are heated on the steam bath, treated with A. R. hydrogen peroxide, combined, and, after filtering off any sulphur, made up to 100 ml. An appropriate aliquot of this solution is used for iron determination (Scott, 1941).

Results.—As only a brief abstract of the paper of Galabutskaya and Govorova (1934) was obtainable, a check upon optimum conditions of temperature, time of extraction, pH, etc., was carried out, using clays of widely different mineralogical composition. The temperature of extraction seemed to have little influence on the amount of iron removed provided several extractions were given, but longer times of extraction were necessary at the higher pH values; the optimum conditions for pH 5·8 are those detailed above.

The effect of the pH of the extracting solution upon various soil clays and pure clay minerals was estimated by comparing the cation-exchange capacity (c.e.c.) of the clays before and after treatment. It was noted that the c.e.c. of each clay after treatment was independent of the pH of the sodium hydrosulphite solution. For some clays (see Table 1) the c.e.c. decreased after treatment, but, as this

Table I.

Effect of sodium hydrosulphite extraction (at pH 5·8) upon c.e.c. of clays.

Clay	Fe_2O_3 removed (%)	C.e.c. (m.e./100g.)	
		Untreated	Treated
30213	7·89	30·0	29·0
47361	6·26	31·8	24·6
54524	6·64	32·6	23·1
Kaolinite...	0·03	3·13	2·99
Illite	0·89	29·9	29·0
Montmorillonite ...	0·35	104·2	108·2
Hydrobiotite	0·30	100·2	99·8

occurred even at pH 6·8 it seems doubtful whether it should be attributed to clay mineral decomposition. The pH range 5·8-6·0 seemed most satisfactory for general use and the results obtained at this pH are given in Table 1. The effect of 0·05 N hydrochloric acid upon various clay minerals was similarly examined, and no appreciable decomposition was observable.

Three clays (illitic, vermiculitic, and montmorillonoidal) were chemically analysed by semi-micro methods (Guthrie, 1933) before and after treatment, and the constituents removed calculated. The results indicated that, generally, (*a*) the acid ammonium oxalate extraction in sunlight removes most iron oxide, but also appeared to cause most clay decomposition; (*b*) the aluminium-ammonium tartrate extraction is very inefficient for some soil clays; (*c*) the sodium hydrosulphite method gives good iron oxide removal without being unduly destructive on clay minerals.

Conclusions.—The hydrosulphite method appeared to be the best of those tested because: (*a*) removal of iron oxides is satisfactory;

(b) extraneous factors, such as availability of sunlight, are not involved; (c) only inorganic reagents are used and laborious treatment before iron determination is thereby avoided; (d) it is applicable to all soil clays tested; (e) there is no undue destruction of the clay minerals; (f) it is relatively rapid; (g) very few precautions are necessary, apart from those common to all micro-techniques.

In conclusion, it may be noted that any organic matter removed from the clay during extraction is readily oxidised during the hydrogen peroxide treatment and does not interfere with the iron determination.

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Discussion.

Mr I. H. Warren.—(1) Have the authors ever used sulphoxylates, which are considerably more stable than hydrosulphites? (2) At one point it was mentioned that a flocculent red precipitate came down and it was suggested this was ferric hydroxide; surely ferric hydroxide cannot precipitate in reducing solution.

Mr B. D. Mitchell and Dr R. C. Mackenzie.—(1) Sulphyoxylates have not been employed as we have found the hydrosulphite method quite satisfactory for our work.   (2) The precipitation of (ostensibly) ferric hydroxide occurred on heating, on the steam-bath, an extract containing only a *very small* amount of sodium hydrosulphite and a *large* amount of iron; our interpretation is that the iron remained in solution while in the reduced state but as soon as oxidation occurred on heating, the ferric salts hydrolysed and $Fe(OH)_3$ precipitated; ferric hydroxide was not therefore precipitated in reducing solution.

Mr R. H. S. Robertson.—Zinc dithionite is easily produced *in situ* by adding zinc dust to the clay and passing SO_2 through; this method might be worth study since it is used in commerce to remove haematite.

Mr Warren.—I believe zinc dithionite is a very efficient agent for iron oxide removal.

Mr Mitchell and Dr Mackenzie.—From the remarks of Mr Robertson and Mr Warren it certainly seems as if an investigation into the use of zinc hydrosulphite (or dithionite) might be quite worth while.   Our only objection is the use of gaseous SO_2 in the laboratory when the sodium salt is available in the crystalline state.

Mr D. A. Holdridge.—I could not reconcile the name sodium hydrosulphite with the formula presented. On reading the abstract I was under the impression that the reagent used was sodium bisulphite.

Mr Robertson.—The compound $Na_2S_2O_4$, though called sodium hydrosulphite by the trade, is more accurately named sodium dithionite.

Mr Mitchell and Dr Mackenzie.—One must, unfortunately, agree with Mr Holdridge that the nomenclature of the complex sulphur salts is rather confusing—indeed it is difficult to find two authorities who agree. Mellor[1], for example, uses "sodium hydrosulphite" for $NaHSO_3$ and "sodium hyposulphite" for $Na_2S_2O_4$. While the latter is frequently given as an alternative name for $Na_2S_2O_4$, the usual name for the former is "sodium bisulphite" and only in Mellor have we seen "sodium hydrosulphite" applied to it. As $Na_2S_2O_4$ is normally referred to, in commerce, as "hydrosulphite" we thought it preferable to use this nomenclature, although "di-thionite," as suggested by Mr Robertson, is undoubtedly the most logical name generically.

Dr G. Nagelschmidt.—Does the method proposed lead to the de-composition of iron-bearing clay minerals, such as glauconite, chamosite or nontronite?

Miss M. J. Deudon.—Hydrosulphite has proved too strong a re-ducing agent to be used with success in presence of ferrous iron.

A sample containing iron-rich chlorites, mixed with siderite and ferric hydroxides, was leached with hydrosulphite in order to remove the ferric iron, with the following results:

	Actual values before leaching	Actual values after leaching	Calculated results[3]
FeO ...	39·5	50·2	45·8
Fe_2O_3 ...	13·8	0·8	—

This seems to prove that hydrosulphite partly removes ferric iron, and partly reduces it to the ferrous state.

Mr B. D. Mitchell and Dr R. C. Mackenzie.—From our experiments it would appear that ferriferous aluminosilicates are, partially any-way, attacked by hydrosulphite. However, this is hardly surprising and when one considers the strain set up in the lattice[2] by the sub-stitution of Fe^{3+} for Al^{3+} it seems to us that such minerals would probably be much more susceptible to attack than the probably highly-aged iron oxides with which they may be associated. The results quoted by Mlle. Deudon are of considerable interest in this connection.

[1] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," London, 1930. Vol. 10, pp. 181 and 267.

[2] R. C. Mackenzie, R. Meldau and R. H. S. Robertson, *Ber. dtsch. keram. Ges.*, 1952, **29**, 221.

[3] Note that $45·8 = 39·5 \times \dfrac{100}{86·2}$ [Ed.]