Determination of live clay in foundry greensand by sodium-selective electrode

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The rapid determination of 'live' clay in greensand is an essential procedure for the efficient running of a foundry production line, since progressive calcination of the clay binder during casting affects mould competence and quality of finish. A new method for assessing the active fraction of clay in foundry sand is described that is based on the response of an ion-selective electrode (ISE) to sodium ions liberated from the clay by ammonium ions. The method possesses advantages of speed and objectivity over the Methylene Blue titration method presently employed in foundries. Results appear to be unaffected by the presence of coal dust in greensand.

1 Introduction

Natural smectite clays, especially sodium montmorillonite or sodium-exchanged Ca–Mg smectites, are used extensively in the production of the greensand moulds employed in many foundries. Fresh, moist clay ('live' clay) allows greensand to flow around a pattern while imparting both the compressive and tensile strengths needed to maintain the mould shape.[1] After casting, clay in the proximity of the hot metal is degraded, causing these properties to be lost. This is termed 'dead' clay. Consequentially, there exists the need to constantly bleed off part of the greensand process stream and to replace it by fresh material, in order to maintain mould performance.[2] To date, this waste has been consigned to landfill, or to alternative use. These options may, however, attract a financial penalty and there is an increasing interest in the possibility of recycling clay binders, in order to achieve significant reductions in operating costs. Rapid analysis of the amount of live clay in greensand wastes would be an essential component of such a process.

The current method utilised for the analysis of live clay is the Methylene Blue 'halo' test.[3] Methylene Blue (MB), a cationic dye, is sorbed strongly by clay particles until the cation exchange capacity (CEC) of the clay is reached, after which the excess remains in solution.[4] In practice, MB is titrated against a known weight of greensand, dispersed in aqueous suspension. Aliquots of 1 cm³ of dye solution are usually added, after each addition of which a drop of suspension is removed and 'spotted' on to filter paper. MB present in excess of the CEC results in the formation of a halo of colour around a central area of dyed clay particles. The first appearance of the halo may be subtle, and some skill is required in order to consistently detect it. In addition, this procedure is slow, prone to subjective error, and accuracy is furthermore limited by the strength of MB solution used and the volume of each aliquot added. The present study suggests that use of an electrode sensitive to sodium ions in solution could provide an alternative, objective method for the quantification of live clay in greensand.

The sodium-selective electrode has found use in many applications, for example in the analysis of foodstuffs,[5] the determination of feldspars,[6] and in the study of the rate of cation exchange on clay minerals.[7] The electrode incorporates a sodium-containing glass membrane, whose electrical potential (E), when placed in contact with an aqueous solution containing sodium ions, is described by the Nicolsky–Eisenman form of the Nernst equation:

$$E = E^0 + (2.303RT)/F \log_{10} (a_{Na^+} + \Sigma k_{Na^+,B}\, a_B^{1/n_B}) \quad (1)$$

where E^0 is the standard potential, R the gas constant, T the absolute temperature, F the Faraday constant, a_{Na^+} the sodium ion activity, and a_B the activity of an interfering ion B, with charge n_B.

The potentiometric selectivity coefficient $k_{Na^+,B}$ expresses the degree of selectivity of the sodium electrode with respect to an interfering ion B. When selectivity coefficients are much less than unity for all other ions present in solution, the electrode response is Nernstian and a plot of potential *versus* sodium ion activity has a slope equal to 59 mV per decade at 298 K. Addition of an electrolyte of non-interfering ions at high ionic strength ensures that the activity coefficient of sodium ions in solution is effectively constant, so that the observed potential is given by:

$$E = E^0 + S \log_{10} [Na^+] \quad (2)$$

where S is the response of the electrode, normally reported as mV per molar decade.

In the present study, the required ionic strength was provided by the addition of a solution of ammonium chloride and ammonium hydroxide (referred to as the Ionic Strength Adjuster or ISA), made up according to the recommendations of the electrode manufacturer. The ISA solution additionally fulfilled the purpose of adjusting the analyte to *ca.* pH 9 (hydrogen is an interferent ion), whilst simultaneously supplying ammonium ions which displace sodium ions from the clay matrix.[8] As ammonium ions show a low level of interference for the sodium electrode (selectivity coefficient *ca* 1×10^{-4})[9] they have a negligible effect on the observed potential even in solutions where their concentration exceeds that of sodium. The response of the sodium-selective electrode is therefore governed only by the concentration of the displaced sodium ions and hence the amount of live clay present in a sample of foundry sand.

2 Experimental

The electrode assembly consisted of a sodium-selective electrode in combination with a calomel reference electrode

(Russell type 97-7129; Russell pH Ltd., Auchtermuchty, Scotland). A high precision digital pH/mV meter (Radiometer PHM84, Radiometer A/S, Copenhagen, Denmark) was used for the potentiometric measurements. A stock solution of ISA was prepared by dissolving reagent-grade ammonium chloride (20 g) in purified water (*ca*. 50 cm³; Elgastat UHQ II, specific resistivity 18 MΩ cm⁻¹), to which 27 cm³ of concentrated ammonia solution (specific gravity 0.880) was added, before making up to a final volume of 100 cm³ with purified water.

The electrode was calibrated using solutions containing 0.001, 0.01, 0.1, 1 and 2 mol dm⁻³ NaCl. A plot of E against $\log_{10}[Na^+]$ was linear ($R^2 = 0.995$) with a gradient of 62 mV per molar decade, compared to the theoretical Nernstian slope of 59 mV. When not in use, the electrode was kept immersed in a storage solution of 5 mol dm⁻³ NaCl. After the electrode had been allowed to equilibrate for three days in the storage solution, repeated checks on the calibration showed the response to be sufficiently reproducible for recalibration to be unnecessary before each set of determinations.

Analyses were performed on a Mediterranean soda-activated montmorillonite, as used by a local foundry. The CEC for this product was specified by the original supplier as *ca*. 90 meq 100 g⁻¹, of which 80–84 meq 100 g⁻¹ were due to Na⁺ ions. 'Dead' clay was produced by heating live clay, in a platinum crucible, placed in a muffle furnace at 850 °C for five hours. Measurements of CEC for dead clay revealed very low values (< 0.001 meq 100 g⁻¹), indicating that the product was comparable to that obtained from a foundry. Samples of simulated foundry greensand, produced by the dry mixing of sand (*ca*. 70% w/w), coal dust (*ca*. 20% w/w) and clay (*ca*. 10% w/w), were representative of those used in practice.

2.1 Determination of CEC

A series of suspensions of clay (*ca*. 0.1 g, accurately weighed) in acidified water (20 cm³) was prepared, containing increasing volumes of 1% (w/v) MB dye solution. Each sample was shaken continuously for ten minutes and then allowed to settle. An aliquot (1 cm³) of the clear supernatant was removed and the dye concentration determined spectrophotometrically ($\lambda_{max} = 663$ nm), from a previously acquired calibration curve. Dilution of the supernatant was necessary at higher concentrations of MB to ensure that the measured absorbance was within the calibration range (<2 absorbance units). Initial addition of dye, at levels below CEC, resulted in irreversible physical adsorption,[4] with no dye detectable in the supernatant. Larger volumes of dye solution resulted in an excess of dye remaining in the supernatant, the concentration of which was then quantified.

The sodium exchange capacity of another sample of the same clay was then determined by ISE. Aliquots (1 cm³) of ISA solution (stock ISA diluted 1 + 99 v/v; 0.077 mol dm⁻³, pH 12) were titrated into a suspension of an accurately weighed (*ca*. 1 g in 50 cm³ water) sample of clay. The potential developed by the electrode was measured after the addition of each aliquot and the amount of sodium ions in solution calculated.

2.2 Determination of clay in greensand

A sample of greensand (*ca*. 5 g, accurately weighed) was suspended in water (50 cm³) and simmered for *ca*. 20 min, in order to ensure complete disaggregation of particles and to allow the clay to dilate. The solution was then acidified (H₂SO₄, 2 mol dm⁻³, 1 cm³), and allowed to cool to room temperature, before titration with MB solution in aliquots of 1 cm³.

Samples for ISE analysis (*ca*. 5 g) were accurately weighed into a 100 cm³ beaker, a solution of ISA (1 cm³) in deionised water (50 cm³) added, and a suspension formed by stirring magnetically for two minutes. The sodium-selective electrode was then immersed in the suspension and the equilibrium voltage recorded. In order to determine whether sufficient ammonium ions had been added to displace all sodium ions from the clay, a further aliquot of 1 cm³ of ISA was added and the potential of the electrode remeasured. No significant change was observed, indicating that complete exchange had been achieved.

In order to compare the two methods, mixtures (*ca*. 10 g, accurately weighed) of simulated foundry greensand (sand, coal dust and live clay) were prepared with different clay contents: 0, 1, 3, 5, and 10% (w/w), comparable to those found in actual foundry greensand. Each sample was then divided into two *ca*. 5 g sub-samples. Sodium determination by ion-selective electrode was carried out on one sub-sample, while the other was subjected to the MB halo test.

The determination of live clay in simulated greensand was then extended to sands containing both live and dead clays. Two series of samples (*ca*. 10 g) were prepared, one by mixing 20% coal dust, 10% total clay, and 70% sand, and the other 20% coal dust, 5% total clay and 75% sand. The clay fractions contained 0, 20, 40, 60, 80, and 100% (w/w) live clay, the balance being made up by dead clay. Again, an attempt was made to prepare mixtures representative of those which might be encountered in foundry operations. Samples were thoroughly dry mixed, by intermittent shaking over a period of 24 h, and then separated into two *ca*. 5 g sub-samples. After dispersion in ISA solution, a sodium ion determination by ion-selective electrode was carried out for both sub-samples.

3 Results and discussion

3.1 Cation exchange capacity by MB sorption

Fig. 1 shows the results of the determination of CEC for live clay by MB sorption. For low levels of added MB, the amount of dye sorbed by the clay was always equal to the amount added. This equality was maintained until the clay became saturated at the CEC, after which the amount sorbed remained constant with the excess MB appearing in the supernatant.[4,10] The CEC determined by this method was calculated to be 80 ± 2.5 milliequivalents (meq) 100 g⁻¹ of clay, in reasonable agreement with the manufacturer's specification of *ca*. 90 meq 100 g⁻¹.

3.2 ISE determination of sodium exchange capacity

The sodium exchange capacity (meq 100 g⁻¹ of clay) of the live clay was obtained from the plot shown in Fig. 2. Titration of the clay suspension by diluted ISA solution resulted in sodium ions
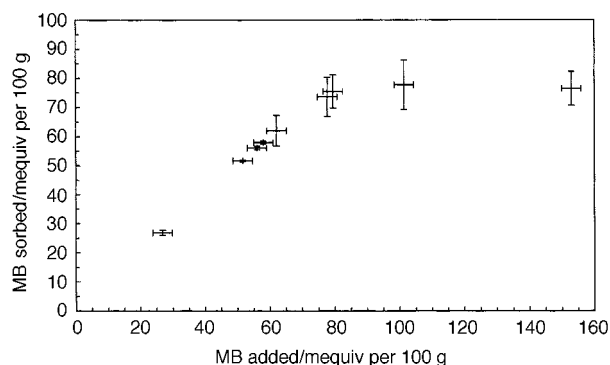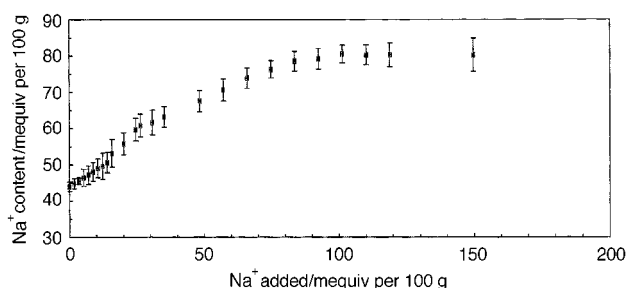

Fig. 1 Spectrophotometric determination of CEC of a Mediterranean soda-activated clay, utilising Methylene Blue (MB) sorption. Error bars denote the standard deviations obtained from four independent determinations.

being displaced from the clay until a constant concentration of sodium ions in solution was reached as indicated by a constant electrode potential, indicating that no more were available for exchange. The sodium exchange capacity was calculated to be 80 ± 3 meq 100 g^{-1}, in agreement with the CEC value resulting from the MB determination. The plot also indicates that about 45 meq 100 g^{-1} of sodium ions were released from the clay into the suspension, prior to the addition of ISA, probably as a result of exchange with protons.
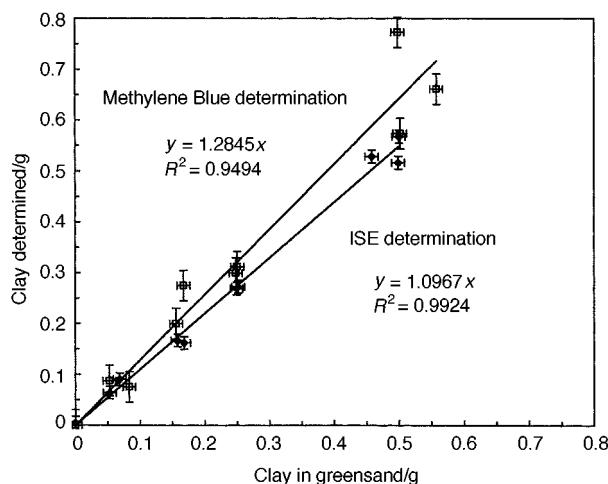
3.3 Determination of live clay in greensand: comparison of MB and ISE methods

A comparison of the results for live clay in simulated greensand as determined by the MB halo test and by ISE is presented in Fig. 3. Both methods give linear correlations between estimated clay content and known clay content, but the ISE method was superior in both accuracy and precision. For the MB results the slope of the plot was 1.2845 ($R^2 = 0.9494$) compared with a slope of 1.0967 ($R^2 = 0.9924$) for the ISE results. A perfect correlation would obviously result in a slope of 1.0000 ($R^2 = 1.0000$).

The results from ISE analyses of simulated greensand mixtures containing both live and dead clay are displayed in Fig. 4, where percentage live clay is plotted against concentration of sodium ions in solution. A linear relationship is observed, with $R^2 = 0.997$, indicating a consistent efficiency of exchange of sodium with ammonium ions. A sodium ion concentration of *ca.* 0.5 ppm was detected in samples containing no live clay, and therefore would appear to represent a lower limit to the detection of sodium in greensand. It is felt

Fig. 2 Determination of sodium exchange capacity of a Mediterranean soda-activated clay, utilising a sodium-selective electrode. Error bars indicate standard deviations obtained from four independent determinations.

Fig. 3 Comparison of results obtained from determination of live clay in simulated greensand mixtures, by ISE and MB halo tests.
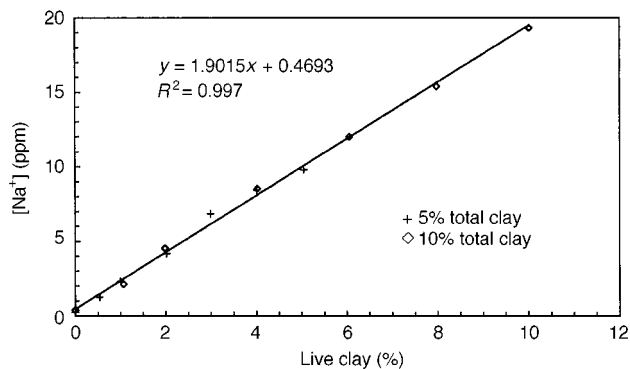
Fig. 4 Sodium ion concentrations in suspensions of simulated foundry greensand mixtures, determined by ISE.

most unlikely, however, that these levels of sodium ions would be encountered during normal foundry operations.

4 Conclusion

The use of a sodium-selective electrode for the determination of live clay in foundry greensand offers several advantages over the traditional method based on uptake of dye. Users of sodium montmorillonite, or sodium-modified clays, could benefit from the objective nature of the analysis which leads to increased accuracy and precision over the MB halo test. The ISE method, which possesses a detection limit adequate for all foundry situations, allows an analysis to be performed in a few minutes, in contrast to the much slower MB halo test. The sodium-combination electrode is robust, simple to use, and requires only an inexpensive voltmeter for its operation. The technique could be modified for use outside the laboratory to give rapid determinations of live clay in the foundry.

In foundries employing clays for which exchangeable cations are only partially replaced by sodium, frequent calibration would have to be carried out in order to compensate for variations in sodium content. Alternatively, dual analysis using both sodium- and calcium-selective electrodes (for sodium-beneficiated calcium montmorillonites) could be used to monitor variations thus providing a method for in-house quality control of the raw material.

References

1 I. E. Odom, *Phil. Trans. R. Soc. Lond.*, 1984, A**311**, 391.
2 W. B. Parkes, *Clay Bonded Foundry Sand*, Applied Science Publishers, London, 1971, pp. 117–124.
3 D. F. Knight, W. Amos, M. H. Lavington and R. Wootton, *Meehanite Sand Control Manual. Green Sand Systems*, Meehanite Institute of Great Britain, International Meehanite Metal Co. Ltd., Reigate, UK, 1992, pp. 3.32–3.34.
4 P. T. Hang and G. W. Brindley, *Clays Clay Minerals*, 1970, **18**, 203.
5 F. G. McNerney, *J. A. O. A. C. Int.*, 1976, **59**, 1131.
6 J. H. Puffer and R. S. Cohen, *Chem. Geol.*, 1975, **15**, 217.
7 V. C. Kennedy and T. E. Brown, *Clays Clay Minerals*, 1964, **13**, 351.

8   E. Grim, *Clay Mineralogy*, McGraw-Hill Book Company, New York, 2nd edn., 1968, pp. 184–233.

9   P. L. Bailey, *Analysis with Ion-selective Electrodes*, Heyden, London, 2nd edn., 1980, pp. 70–71.

10 G. W. Brindley and T. D. Thompson, *Israel J. Chem.*, 1970, **8**, 409.

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