Tests of Activation of Clays and the Effect of Activation on Casting Quality

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ABSTRACT
A commercial sample of good quality bentonite from the western United States was tested for its amenability to activation by sodium carbonate and sodium pyrophosphate. Tests of liquid limit, viscosity and wet strength all indicated that the bentonite could be improved by adding controlled amounts of sodium carbonate. Laboratory tests showed that, for optimum activation, equivalent weights of sodium carbonate or of sodium pyrophosphate could be used. Sodium bicarbonate, which would be expected to be formed in the mold, deactivated the bentonite. Disodium orthophosphate, formed by the hydrolysis of sodium pyrophosphate, was almost neutral to this particular bentonite. Two series of 10 heats, 500-lb each, in which sand was repeatedly used to make SFSA (Steel Founders Society of America) sand blocks, were made, using unactivated bentonite and bentonite activated with sodium carbonate. The activated material produced fewer scabs and required no additions of re-bonding bentonite. Two further series of 20 heats each were made, using 100-lb sand blocks. Bentonite additions were controlled by the molybden blue test. The activated sand produced better castings and required smaller clay additions. After 12 heats with the activated sand, the liquid-limit test indicated that hydrated lime was more effective than sodium carbonate in reactivating the sand. This is attributable to its conversion of sodium bicarbonate to sodium carbonate. After about 10 heats, further additions of re-bonding bentonite were about the same for the 2 series. It is concluded that, if a sample of western bentonite can be activated, it is advantageous to do so.

Introduction—From time to time, reports have been issued on the use of activation to improve the foundry performance of bentonite from the western United States.\(^1\)\(^2\)\(^3\) However, this practice is not widely used in North American foundries, although it is used in some western bentonite manufacturing operations. There are probably several reasons for the lack of acceptance of activation by North American foundries:

1) bentonites from the western United States appear to be superior in the unactivated state, to European bentonites;
2) activation lowers the dry strength and refractoriness of the sand. This would be likely to result in erosion and increased burn-on because of fusion;
3) the activating chemicals, usually soda ash or sodium pyrophosphate, are subject to deterioration by mold gases or heat;
4) not all western bentonites are amenable to activation; and
5) there is a feeling that, if a bentonite is amenable to activation, this is an indication that it is of inferior quality; i.e., there is something lacking in its natural makeup. Most work with activation has been done in an effort to upgrade inferior bentonite.

This investigation was undertaken to determine whether a good quality western bentonite, amenable to activation, would give a better performance after it had been activated. The bentonite used was from the western United States, from the same lot used for the work described in a previous report.\(^4\)

Laboratory Tests

Tests for Activation—In a study of the activation of Bavarian bentonites, R. Fahn\(^1\) found that the optimum degree of activation could be determined by measuring the viscosity on a Banovier viscometer. The optimum activation, obtained when the viscosity reached a maximum, correlated with the best durability, as measured by the green compressive strength of sand mixtures heated to 500°C (950°F) for 1/2 hr., and with the casting results. Fahn obtained much better results when the bentonite was "properly activated" before it was used than when soda ash was only mixed with it.

He also found that viscosity results obtained immediately after the clay was activated did not correspond to those obtained the next day. Hence, he recommended that the activated bentonite be allowed to stand overnight before measuring the viscosity. The observation that activation takes some time was confirmed by our work, and we, too, recommend overnight standing before testing for activation.

In addition to viscosity, 2 other tests that have been found to correlate with bentonite quality are prospective tests for amenability to activation. These are the liquid-limit test, standard foundry test for bentonite, and the wet-strength test, which Boenisch used to measure activation.\(^7\)

The effects of soda ash on the sand of the sample of bentonite under study as reflected on the viscosity and liquid limit and on the wet strength of the sand mixtures, are shown in Fig. 1. Viscosities of slurries containing 8 lb bentonite to 100 cc water were measured at 600 rpm on a Banovier viscometer, with the instrument set up as for drilling mud. Wet tensile strengths were measured at room temperature, on mixtures with a sand/bentonite ratio of 150/0.5, at 8% moisture. The liquid-limit test indicated a minimum at a lower sodium carbonate content than did the other 2 tests. The sodium carbonate requirement for the viscosity test was probably increased by its lower concentration, as a result of the thinner slurry. The sodium carbonate in the sand mixture probably reacted with aluminum and the silicon dioxide to produce sodium bicarbonate. The large surface area of the sand grains would provide an opportunity for this to occur.

Deterioration of Activator—Sodium carbonate and sodium pyrophosphate undergo reactions with the following:

\[
\text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{NaHCO}_3, \quad (1)
\]

\[
\text{Na}_3\text{P}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{Na}_2\text{HPO}_4, \quad (2)
\]

The effects of these reactions on the activation of a bentonite sample, as denoted by liquid limit and pH tests, are shown in Fig. 2. Sodium carbonate that has been changed to sodium bicarbonate must be replaced by new soda ash. Sodium bicarbonate remains as a contaminant and deactivates the clay. The tests also show that pH values cannot be used to control the activation of bentonite.

Disodium orthophosphate, formed by the hydrolysis of sodium pyrophosphate, has almost no effect on the activation of this sample of bentonite. (Disodium orthophosphate deactivates some bentonites.) In this sample any of the hydrolyzed sodium pyrophosphate would have to be replaced, although it was not deactivated by the added soda ash.

Equivalent weights of sodium carbonate and of sodium pyrophosphate are required and the effect on the activation is the same. The equivalent weight of sodium pyrophosphate is about 1.25 times that of soda ash and the price is about 6 times as great. Hence, soda ash would be the cheaper material to use.

Foundry Tests

SFSA (50-lb) Scab Block—The previous tests on this sample of bentonite in the unactivated state included a series of 10 heats, in which the bentonite-bonded sand was re-bonded with additional bentonite to maintain a constant green compressive strength.

To test the effect of activation, 2% sodium carbonate, based on the weight of the bentonite, was added in solution with the tempering water. Sodium carbonate was effective for this test and found in solution, whereas Fahn\(^7\) found that it was relatively ineffective when added to the bentonite in powder form. Soda ash, added as a fine powder with the water before the bentonite, increased the wet strength of test sand mixtures and may have worked as well in practice as it did by adding in solution.

The sand mixture, preparation method and molding and pouring procedures were the same as described in the previous report.\(^4\)

The sand was round-grained, AFS fineness 55, from Ottawa, Illinois.

Six batches of sand were mixed in a 3-1/2 sand muller:

150 lb sand
Testes de Ativação de Argilas e o Efeito da Ativação na Qualidade dos Fundidos.

- São testadas argilas com carbonato de sódio e Pirofosfato de sódio, através de testes como: limite líquido (?), viscosidade e o R.I.V.
- O Bicarbonato de Sódio que se forma no molde, pela destilação do CaCO₃ desativa a bentonita, já o Disodio Pirofosfato, formado pela hidrólise do Pirofosfato de Sódio é neutro.
- A ativação química normalmente Barrita (CaCO₃) ou Pirofosfato de Sódio, estão sujeitos a deterioração pelos gases ou calor do molde. O que mais fácil de ativar uma bentonita, menor é sua qualidade.

**TESTES DE LABORATÓRIO**

- **DE FUNDIÇÃO**
  - Avaliação dos Fundidos
  - Deterioração do Ativador
  - Controle de Bentonita e Ativador.
muddled 1 min
passed through aerator.
For coarse the sand, including the scale which resulted from the castings, was processed in 5 batches:
175 lb used sand
3.5 oz gelatinized corn flour
muddled 1 min
moisture to give 75 moldability, after
aeration, plus soda ash in solution as
required by rebonding bentonite.

mulled 1 min
reebonding bentonite addition
mulled 4 min
final moisture adjustment
mulled 1 min
passed through aerator.

The test casting was the scab block developed by the Steel Founders' Society of America. The molds were rammed by a pneumatic hand rammer to a mold hardness of C90, as measured on the Dietert mold-hardness tester.

Mild steel (0.20% C from basic arc furnace) was used for the castings. Initial pouring temperatures ranged between 295°F (162°C) and 300°F (160°C). There was a temperature drop of about 20°F (10°C) between molds. Pouring time was 8-10 sec. The castings were shaken out 1 hr after they were poured.

Bentonite Additions—The bentonite additions required for the 2 series are shown in Fig. 3. The series containing the activated clay required no bentonite or activator additions, which indicated that it had better durability.

Evaluation of Castings—The evaluation of test castings was based on the area of scabbing on the plate surfaces. Scabs were rated in four groups as follows:

rating 1: 0-½ in.
rating 2: ½-1 in.
rating 3: 1-2 in.
rating 4: 2 in. and over.

Representative casting from the 2 series with unactivated and activated bentonite are shown in Figs 4 and 5. Photographs for the unactivated series are shown in Fig. 1 in a previous report. The ratings for scabbing and surface finish were shown in Fig. 6 and 7. The 2 series had about the same surface finish, but the activated series scabbled much less.

Sand Properties—Sand properties obtained with the 2 series are compared in Figs 8 and 9. Activation enhances the effective clay content, as defined by Helbe et al., and also the hot wet strength, but lowers the dry strength.

Deterioration of Activator—After the 10th heat the activated sand was tested with further additions of sodium carbonate and a maximum value was obtained for wet tensile strength (tested at room temperature with 0% moisture) with an addition of 0.002%, based on the sand. This indicates that because of the conversion of sodium carbonate to the bicarbonate and larger additions could have been used.

Tests with 200-lb Scab Block—The tests with the SFSA scab block indicated that with castings from the large proportion of the bentonite was beneficial. The possibility remained that with larger castings the desired deleterious effects of lower dry strength and increased fusion of the sand, caused by the addition, would more than offset the beneficial effects and make the castings worse. Another possibility was that burn-out of the sand by the large castings would increase the tendency to form pinholes on small castings. Two further series, of 20 heats each, were made to test these possibilities.

Test Castings—For the large casting, the size of the scab block was increased, as shown in Fig. 10. This casting, with the gate, weighed 202 lb. To test for the formation of pinholes a 2 x 6-in. cylindrical casting, with the gate, weighed slightly over 20 lb, was used. No pinholes were observed on any of the castings, but sand inclusions and small cracks (crazes) occurred more frequently after the sand had been repeatedly used.

Test Procedure—Each heat included 2 scab blocks and 1 cylinder, with a total weight of about 425 lb. After 20 heats, the sand had been used to cast over 10 tons of metal per ton of sand, or the equivalent of 6.5 tons of finished castings per ton of sand. In 5 heats, 160-lb batches were used.

The molds were rammed to 90 mold hardness and poured in mild steel at about 295°F (162°C) to 300°F (160°C) in 20-25 sec. They were shaken out 2 hr after they were poured.

Conclusion of Bentonite and Activator—In these series the bentonite additions were controlled by the methylene-blue test. Because the tests for the previous series with the SFSA scab block had shown that 2.5% addition of sodium carbonate was not enough, this was raised to 3% for the activated sand of the new series.

After 6 heats, liquid-limit tests of the sand (made on muds containing 30 g. water and 105 g sand) showed that it was becoming overactivated. The requirement of the activator was estimated by the number of joint required to close the standard notch of the lost to a length of ½ in. Between the 7th and 12th heats sodium carbonate was added or omitted according to the results of this test. After 12 heats the liquid-limit tests showed that hydrated lime was more effective than sodium carbonate in improving the liquid limit of the sand:

$$\begin{align*}
2NH_4CO_3 &+ Ca(OH)_2 \rightarrow \\
Na_2CO_3 &+ CaCO_3 &+ 2H_2O
\end{align*}$$

(F)
Thereafter, 10-15 g of hydrated lime were used to reactivate a 100-lb batch of sand. This was added with the tempering water.

The absorption by 5-g samples of sand, and by centrifuged samples (colloidal clay test)\(^1\) of a 1% solution of methylene blue, is shown in Fig. 11. The decreased methylene-blue adsorption by the activated sand should indicate that the activation has impaired the clay. However, the test procedure requires the addition of sulfuric acid. Sodium sulfate, produced by the reaction between this and the sodium carbonate that was added for activation, deactivates the sand. When the test is made without the addition of sulfuric acid, the adsorption of methylene-blue is increased by the optimum activation.

The bentonite additions made to the 2 series are shown in Fig. 12. Activation at first reduced the bentonite requirements, but after about 10 heats, further additions to the 2 series were about the same.

**Evaluation of Castings**—The sand deteriorated with use so that after about 15 heats with the unactivated bentonite and 19 heats with the activated series 1, it probably could not have been used to make good castings of any size. In addition to scabs, the incidence of snotter and sand inclusions increased. On the 17th use with the unactivated series, when the sand contained 5% moisture, a mold reaction occurred in which metal appeared to have boiled against the mold wall to produce a porous surface. On this and subsequent heats blows occurred in the corner between the plate and the block. On the 20th use with the activated sand, localized reaction produced some gas holes on the block.

The sand burned on to the plate progressively more as it was used. This...
Fig. 10. 200-lb scab block.

Fig. 11. Adsorption of methylene blue of sand for 200-lb scab block.

Fig. 12. Bentonite additions for 200-lb scab blocks.

Fig. 13. 200-lb scab block, heat 1, unactivated sand.

Fig. 14. 200-lb scab block, heat 19, unactivated sand.

Fig. 15. 200-lb scab block, heat 12, activated sand.

Fig. 16. 200-lb scab block, heat 19, activated sand.

The burn-on, which could be removed but with increasing difficulty by sand blasting, was especially tenacious on the castings made in activated sand. Five of the castings are shown in Fig. 13-17. Scab ratings are shown in Fig. 18. Scabs which occurred on the block are included in these ratings because these increased in number as the sand was used, whereas the incidence of scabbing on the plate remained fairly constant. Surface finish ratings of the scab plate are shown in Fig. 19.

Sand Properties—Sand properties obtained with these 2 series are compared in Fig. 20-22. Activation did not at first give the expected decrease in dry strength. Initially this was because of the high moisture content, which was used to add the required amount of sodium carbonate solution.

The increase in moisture requirements as the sand was used was less for the activated sand than it was for the untreated sand. The effect of this was evidenced on the castings, which had fewer gas holes and blows than had occurred with the untreated sand at high moisture contents.

The weight of the AFS test specimen decreased as the sand was used. This was undoubtedly because of the formation of a layer of sintered clay on the sand grains—a process known as colloidization. This colloidization, which appears to be more harmful than visible scale particles, accounts for the deterioration of casting quality with sand use. This deterioration occurs even when all known sand properties are maintained at desirable levels.

The weight of AFS test specimens was not a sufficiently sensitive test to distinguish between the amounts of dead-burnt clay in the activated and unactivated series, but the difference in amount probably accounts for much of the superiority of the activated series.
Summary—The amenability of bentonites to activation and the optimum amount of activator can be determined by the liquid-limit test, by a viscosity test or by the wet-torque strength of a sand mixture.

Soda ash and sodium pyrophosphate, the most commonly used activators, are both subject to chemical change by use and the reaction products may deactivate the sand.

Activation by soda ash of a high-quality western bentonite that tests had shown to be amenable to activation resulted in improved castings. Smaller additions of reactivating bentonite were required.

After prolonged use of the sand, sodium carbonate became less effective in activating the reactivating bentonite. Additions of hydrated lime, based on its effect on the liquid limit of the sand, helped to reconvert sodium bicarbonate to sodium carbonate, thus improving the activation of the sand. However, at this point, the reactivating requirements of the activated and untreated sand were about equal.

From the results of this investigation it can be concluded that when tests show that a western bentonite can be activated, it is advantageous to do so.

References