Reclamation of self-setting mixtures with olivine bound with alkaline resols

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Abstract

For the reasons of environmental problems connected with the use of furan binders the attention is increasingly paid to self-setting mixtures with alkali resols. A resol binder stabilized with KOH, NaOH is hardened by liquid esters with the formation of alkaline salts. The increase of their concentration affects the shortening of the mixture bench life, it decreases strength, abrasive wear of moulds and cores is growing, and it results in uneconomical dilution of the reclaim with expensive new base sand. Length of life (bench life) of mixtures plays an important role just in manufacture of huge and voluminous moulds and cores in self-setting mixtures. This contribution aims at analyzing the function of reactive alkaline salts in the reclaim, it monitors consequences of its thermal exposure on properties of self-setting mixtures, and it deals with development of methods evaluating its qualities.

Keywords: innovative foundry technologies and materials; Mechanical properties; Self-setting mixtures; Alkaline resols; Reclamation

1. Introduction

With regard to environmental problems with furan binders the attention is increasingly paid to self-setting mixtures (ST – mixture) with alkaline resols. For alloy steels (Mn – steels) the mixtures are connected with olivine base sand. The resol binder stabilized with KOH, NaOH is hardened by liquid esters with the formation of alkaline salts that are the main subjects of interest when applying both dry mechanical pneumatic reclamation and the thermal one. Their concentration increase (some sources give a critical concentration of 0.16 %) effects the shortening of the mixture bench life, it decreases strength, it increases the abrasive wear of moulds and cores, and it leads to uneconomical dilution of the reclaim with an expensive new base sand. Length of life (bench life) of mixtures plays an important role just in manufacture of huge and voluminous moulds and cores in self-setting mixtures. It can be also controlled by the choice of esters or by water addition but in results in prolongation of the initial plastic state of solidifying moulds and in deformation of cores. Above all there remains an interest in obtaining a “quality” reclaim and application of simple and reliable processes of evaluating its quality.

This contribution analyzes the function of reactive alkaline salts in the reclaim, it monitors consequences of its thermal exposure on properties of self-setting mixtures, and it deals with development of methods evaluating its qualities. The results contribute to orientation in the choice of thermic reclamation processes of self-setting mixtures and achieving an improved economy of the given technology.
2. Materials and methods

2.1. Used raw materials

Chemical composition of new base sand (SIBELCO NORDIC) is summarized in Table 1. (wt. %).

<table>
<thead>
<tr>
<th>Chemical composition of new olivine</th>
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</thead>
<tbody>
<tr>
<td>MgO</td>
<td>49.60</td>
</tr>
<tr>
<td>SiO₂</td>
<td>41.70</td>
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<tr>
<td>Fe₂O₃</td>
<td>7.40</td>
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<tr>
<td>Al₂O₃</td>
<td>0.46</td>
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<tr>
<td>CaO</td>
<td>0.15</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.31</td>
</tr>
<tr>
<td>NiO</td>
<td>0.32</td>
</tr>
<tr>
<td>FeO</td>
<td>6.90</td>
</tr>
<tr>
<td>MnO</td>
<td>0.09</td>
</tr>
<tr>
<td>AlO₃</td>
<td>0.76</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.02</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Mineralogical analysis has shown the presence of 5.36 ± 0.54 weight % Fe²⁺ (fayalite), basic parameters of granulometry (d₅₀ = 0.28 mm), pH = 9.25 and electric conductivity of the extract 71.9 µS/cm under 27.6 °C.

An operation reclaim (METSO Minerals, s.r.o., Přerov) from dry mechanical reclamation of IMF and self-setting mixture:

90 weight parts of new olivine
10 weight parts of the reclaim
1.7 weight parts of Fenotec 280
22 % of the ester hardener (HX60, HX 120) per a binder

Its chemical composition is given in Table 2., d₅₀ = 0.29 mm, pH = 9.98 and electric conductivity of 579 µS/cm under 27.6 °C.

<table>
<thead>
<tr>
<th>Chemical composition of the reclaim of ST – mixture</th>
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</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>45.90</td>
</tr>
<tr>
<td>SiO₂</td>
<td>44.40</td>
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<tr>
<td>Fe₂O₃</td>
<td>6.90</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.76</td>
</tr>
<tr>
<td>CaO</td>
<td>0.13</td>
</tr>
</tbody>
</table>

The Fenotek 280 binder with alkali content of 8.3 % represented in Na/K = 1:1 ratio, pH = 11.6

Ester hardeners:
- „quick-acting“ HX 60 (a mixture of acetic acid esters, glycerol and glycol)
- „slow-acting“ HX 120 (a mixture of acetic acid esters, glycerol, glycol, and butyl alcohol)

An additive for reduction of alkalinity in the reclaim (Thermal Additive ADT – 1, solution)

2.2. Simplified chemist of self-setting mixtures reactions

Esters in strongly alkaline medium of resol hydrolyze:

\[ Ester \rightarrow \text{acid (CH}_3\text{COOH)} + \text{alcohol} \]

Acid, the acetic one above all, neutralizes the alkaline hydroxides with formation of salts,

\[ \text{KOH + CH}_3\text{COOH} = \text{CH}_3\text{COOK} + \text{H}_2\text{O} \]
\[ \text{NaOH + CH}_3\text{COOH} = \text{CH}_3\text{COONa} + \text{H}_2\text{O} \]

it shifts the equilibrium towards the resol formation and the mixture is strengthened.

Under the influence of thermal exposure of the mould the salts (acetates) succumb to changes as follows:

\[ 2\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O} \xrightarrow{\text{400–450°C}} 2\text{CH}_3\text{COOH} + \text{Na}_2\text{CO}_3 + \text{dimethylketone (acetone)} \]

Acetone burns and soda remains. Thus it can be assumed that the return self-setting mixture (the reclaim) contains acetates – CH₃COONa(K) for temperatures lower than 400 °C and carbonates Na₂CO₃ and K₂CO₃ for temperatures higher than 400 – 450 °C. Both the carbonates forms are melted above 851 (891) °C, they form a deposit on grains and in such a way they are transferred in a form extractible with difficulties.

The alkali in the reclaim are then determined as water soluble ones (carbonates, acetates) and general ones containing a portion of badly soluble alkaline melts too.

3. Experimental results and discussion

3.1. Influence of annealing temperature on pH and conductivity of the reclaim

The reclaim of self-setting mixtures was annealed to temperatures of 300, 600 and 900 °C/1 h in air atmosphere. The pH and electric conductivity were determined in a water and base sand suspension (100 g H₂O/10 g sample). Values of pH and conductivity measurements are included in Table 3. and Fig. 1.

<table>
<thead>
<tr>
<th>Conductivity and pH of olivine sand and reclaim</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>sample</td>
<td>pH/ °C</td>
</tr>
<tr>
<td>Olivine sand</td>
<td>9.25/33,2</td>
</tr>
<tr>
<td>Reclaim</td>
<td>9.98/32,6</td>
</tr>
<tr>
<td>Reclaim (annealed at 300 °C/1 h)</td>
<td>10,14/30,3</td>
</tr>
<tr>
<td>Reclaim (annealed at 600 °C/1 h)</td>
<td>10,12/37,9</td>
</tr>
<tr>
<td>Reclaim (annealed at 900 °C/1 h)</td>
<td>8,14/37,9</td>
</tr>
<tr>
<td>Distilled water</td>
<td>5,93/36,4</td>
</tr>
</tbody>
</table>

The olivine base sand is of a slightly alkaline nature (pH = 9.25). The reclaim is slightly more alkaline (pH = 9.98) but only above 600 °C a drop (pH = 8.14) to values lower than that one’s measured for a new base sand was observed. More important changes can be found out for electric conductivity that
is ca 8 times higher in case of the reclaim in comparison with new olivine. Above 300 °C the conductivity considerably decreases almost to values of distilled water (26.9 µS/cm).

Colour changes with annealing temperature are also interesting. The black reclaim (with high content of pyrolysis carbon) after annealing to 300 °C didn’t change its colour. Only under 600 °C it gets green colour of new base sand and after annealing to 900 °C (oxidation of iron) it gets deep red colour.

3.2. Influence of the reclaim annealing temperature on content of total and soluble (extractible) alkali

Two methods were used for determination of alkali:

Methodology – 1: Basic process of silicate analyses. Total decomposition. (Treated CSN 720101 standard)

Methodology – 2: Determination of alkali from the water extract. The filtrate stabilized with HNO₃ and with AAS fiery technique the K and Na elements were determined.

Results of both processes are given in Fig. 2. and Table 4.

The reclaim (initial material) contained 0.11 % Na and 0.14 % K. Total alkali content (K + Na) was 0.40 %. With annealing up to 600 °C no substantial changes were observed, only above 600 °C the extractible alkali portion considerably decreases (< 0.10 %). These changes correspond to results of electric conductivity (Fig. 1.). Conductivity slightly decreases already in the neighbourhood of 600 °C but substantial change takes place under temperatures above 600 °C and under 900 °C. These conclusions wholly agree with done analysis of the chemism in case of hardening reactions.

3.3. Strength properties of self-setting mixtures with a reclaim

The ST –mixture corresponded to given operating composition. Besides using the annealed reclaim (600 °C/1 h) the additive ADT – 1 (1 %) was also checked.

But the reclaim wasn’t deducted after annealing. It results from the course of bending strength that even higher strengths than in case of new olivine were achieved in case of a mixture with annealed reclaim (Fig. 3.).

It is true that the water addition in the mixture (up to 1 %) prolongs the life (bench life) of self-setting mixtures but the hardening rate and strength are decreasing and the initial plastic state increases (Fig. 4.).

With the use of the slow-acting hardener (HX 120) the plastic state was prolonged up to 2 h. Annealing of the reclaim under 600 °C/1 h brings an important effect in increasing the bending strength of the self-setting mixture. The growth after 5 h is cca 40 %, after 24 h cca 62 % (Fig. 5.)
3.4. Analysis of the present process of reclamation of ST – mixtures (Metso, s.r.o. Přerov) and checking the new tests of the reclaim quality

The self-setting mixture with olivine and a resol binder is reclaimed in the foundry on an IMF device (10 t/h) by a cold mechanical wear. For complex evaluation of the reclamation process efficiency the samples — dedusting particles, return mixture, reclaim, self-setting mixture — were taken off in one hour intervals for 12 h, i.e. 48 samples altogether. Samples characterizing the initial state (1), the mid (6) and the end of sampling (12) were chosen from every set and pH and electric conductivity were determined on them (fig. 6.) and water extract alkalinity was determined with use of a new titration method developed by the Mining University – Ostrava University of Technology (fig. 7.).

**Determination of pH:** pH of all 4 sample groups is in the alkaline zone, within the interval of 10.3 – 10.8, i.e. it is higher than of new olivine (pH = 9.27), but without any dependence on the kind of tested material.

**Measurement of electric conductivity:** Unambiguously the highest values were obtained for dedusting particles (3500 – 6150 µS/cm). The return mixture has considerably lower values (700 – 910 µS/cm). As expected the reclaim has even lower ones (675 – 750 µS/cm). Therefore the electric conductivity can be considered one suitable criterion of evaluation the reclaim quality.

Annealing of the reclaim leads to burning of the binder residues and pyrolysis products. Results are without abrasive wear and dusting of the reclaim. A next effect can be expected including a decrease of alkali salts concentration.
3.5. A new method of evaluating the reclaims alkalinity by the Technical university of Ostrava

The question is a combination of titration with solution of 0.1M HCl to a colour indicator (bromphenol blue) in an acid zone with simultaneous measurement of pH (constant value of 4.6 ± 0.05) (Fig. 7.).

3.6. Fracture surfaces of self-setting sands

Monitoring the fracture surfaces of self-setting mixtures with the aid of SEM technique and a microprobe has shown a typical adhesive destruction of binder bridges (Fig. 8.). Uncovered grain surfaces and „dished” binder residues (+) contain considerable portion of pyrolysis carbon and alkali (K, Na) (Fig. 9.). Low adhesion of binder system residues forms a precondition for high efficiency of alkalinity decrease by abrasive wear.

Fig. 6. Electric conductivity of chosen samples

Fig. 7. Measurement of the extract alkalinity with a new process

Fig. 8. Fracture surface of the self-setting mixture (90/10 new olivine; 1.7 weight parts of Fenotek 280; 22 % HX 120 for a binder, water)

Fig. 9. A binder envelope of grains in the reclaim with high concentration of alkali salts
4. Conclusion

Annealing of the reclaim to 300 – 900 °C has shown important changes of its behaviour that was explained by analyzing the chemism of hardening reactions.

With annealing to 600 °C the electric conductivity of water suspension decreases in correlation with the decrease of extractible alkali. At the same time the bending strength of self-setting mixtures considerably increased (± 62 %/24 h).

For the reason of iron oxidation the higher annealing temperatures (often recommended 900 °C) lead to distortion of the real residual binder portion (loss on ignition) and it transfers the salts into an unextractible and difficult to remove form.

A decrease of alkali salts concentration in the reclaim can be achieved as follows:

• By dissolving in water (with water addition the strength decreases and the plastic state is prolonged)
• By an intensive cold wear
• By annealing (600 °C) and an intensive wear
• With the use of special additives

An extensive measurement of samples of dedusting particles, return mixture, reclaim and self-setting mixture from a mixer taken in hourly intervals from the operating reclamation unit has shown high composition variability during 12 hours, low declarative ability of pH measurements but a sufficient sensitivity of measurements of electric conductivity of the extract.

Measurements of the reclaim alkalinity using the new method developed by the Mining University – Ostrava University of Technology with use of the extract titration with the HCl solution to the chemical indicator with the aid of simultaneous checking the pH measurements has been proved suitable with high sensitivity.

Olivine grains in the self-setting mixture reclaim are sharp angular, without appearances of working, from a great surface part free of binder residues where pyrolysis carbon and alkali salt crystals (adhesive destruction of binder bridges) are found.