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Reclamation of Self-Setting Mixtures with Olivine Bound with Alkaline Resols

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Abstract

For the reason of environmental problems connected with the use of furan binders, attention is increasingly being paid to self-setting mixtures using 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 also decreases strength, increases abrasive wear to moulds and cores, and results in uneconomical dilution of the reclaim with expensive new base sand. The length of life (bench life) of mixtures plays an important role in the manufacture of huge and voluminous moulds and cores in self-setting mixtures. This study aims at analyzing the function of reactive alkaline salts in the reclaim, monitors the consequences of its thermal exposure on the properties of self-setting mixtures, and 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 the environmental problems involving the use of furan binders, attention is increasingly paid to self-setting mixtures (ST – mixture) using 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 thermal. Their concentration increase (some sources give a critical concentration of 0.16 %) the shortening of the mixture bench life, decreases strength, increases the abrasive wear to moulds and cores, and leads to uneconomical dilution of the reclaim with an expensive new base sand. Length of life (bench life) of mixtures plays an important role in the manufacture of huge and voluminous moulds and cores in self-setting mixtures. It can also be controlled by the choice of esters or by water addition but results in the prolongation of the initial plastic state of solidifying moulds and in the deformation of cores. Above all, there remains an interest in obtaining a "quality" reclaim and the application of simple and reliable processes of evaluating its quality.

This study analyses the function of reactive alkaline salts in the reclaim, monitors consequences of its thermal exposure on properties of self-setting mixtures, and deals with the 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 a new base sand (SIBELCO NORDIC)was used and is summarized in Table 1. (wt. %).

Table 1.
Chemical composition of new olivine

MgO	49,60	Cr_2O_3	0,31
SiO_2	41,70	NiO	0,32
Fe_2O_3	7,40	MnO	0,09
Al_2O_3	0,46	Na_2O	0,02
CaO	0,15	K_2O	0,03

Mineralogical analysis has shown the presence of 5.36 ± 0.54 weight % Fe^{2+} (fayalite), basic parameters of granulometry (d_{50} = 0.28 mm), pH = 9.25 and electric onductivity 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 a self-setting mixture was used:

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
water

Its chemical composition is given in Table 2., d_{50} = 0.29 mm, pH = 9.98 and electric conductivity of 579 µS/cm under 27.6 °C.

Its chemical composition is given in Table 2., d_{50} = 0.29 mm, pH = 9.98 and electric conductivity of 579 µS/cm under 27.6 °C.

Table 2.
Chemical composition of the reclaim of ST – mixture

MgO	45,90	Cr_2O_3	0,31
SiO_2	44,40	NiO	0,31
Fe_2O_3	6,90	MnO	0,13
Al_2O_3	0,76	CaO	0,13

The following were also used:
The Fenotek 280 binder with an 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 the reduction of alkalinity in the reclaim (Thermal Additive ADT – 1, solution)

2.2. Simplified chemistry of the reactions of self-setting mixtures

Esters in a strongly alkaline medium of resol hydrolyze:

Ester → acid (CH_3COOH) + alcohol (1)

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

$$KOH + CH_3COOH = CH_3COOK + H_2O \quad (2)$$

$$NaOH + CH_3COOH = CH_3COONa + H_2O \quad (3)$$

It shifts the equilibrium towards resol formation and the mixture is strengthened.
Under the influence of thermal exposure of the mould, the salts (acetates) succumb to the following changes:

$$2CH_3COONa \cdot 3H_2O \xrightarrow{-6H_2O} 2CH_3COONa$$
$$2CH_3COONa \xrightarrow{400-450°C} CH_3COCH_3 + Na_2CO_3 \quad (4)$$

dimethylketone (acetone)

Acetone burns, and soda remains. Thus, it can be assumed that the return self-setting mixture (the reclaim) contains acetates (CH_3COONa (K) for temperatures lower than 400 °C and carbonates Na_2CO_3 and K_2CO_3 for temperatures higher than 400 – 450 °C). Both the carbonates are melted above 851 (891) °C, they form a deposit on grains and in such a way they are transferred in a form that is extractable yet difficult.
The alkali in the reclaim are then determined as water soluble (carbonates, acetates) and general (also contain a portion of badly soluble alkaline melts).

3. Experimental results end 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 a 900 °C/1 h in air atmosphere. The pH and electric conductivity were determined in a water and base sand suspension (100 g H_2O/10 g sample). Values of pH and conductivity measurements are included in Table 3. and Fig. 1.

Table 3.
Conductivity and pH of olivine sand and reclaim

sample	pH/ °C	Conductivity [µS/cm]/ °C
Olivine sand	9,25/33,2	71,9/27,6
Reclaim	9,98/32,6	579/27,6
Reclaim (annealed at 300 °C/1 h)	10,14/30,3	589/27,6
Reclaim (annealed at 600 °C/1 h)	10,12/37,9	453/29,9
Reclaim (annealed at 900 °C/1 h)	8,14/37,9	47/29,5
Distilled water	5,93/36,4	26,9/23,3

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 those measured for a new base sand were observed. More important changes can be found for electric conductivity that is ca 8 times

higher in the case of the reclaim in comparison with new olivine. Above 300 °C the conductivity decreases considerably to values close to those of distilled water (26,9 μS/cm).

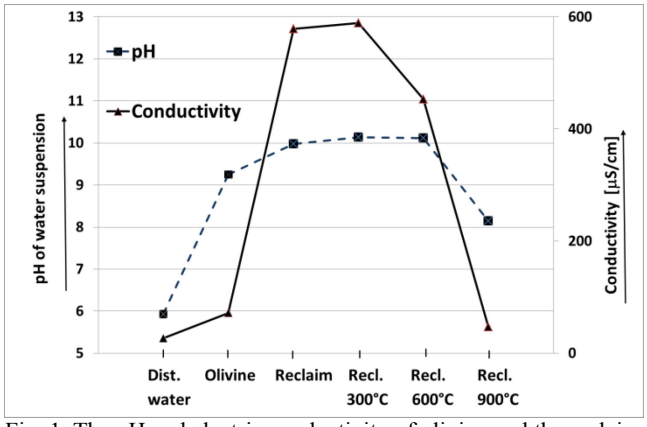


Fig. 1. The pH and electric conductivity of olivine and the reclaim

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 took on a green colour of new base sand, and after annealing to 900 °C (oxidation of iron) it took on a deep red colour.

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

Two methods were used for the 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 was stabilized with HNO_3 and the K and Na elements were determined using AAS.

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 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 analysis done of the chemism in case of hardening reactions.

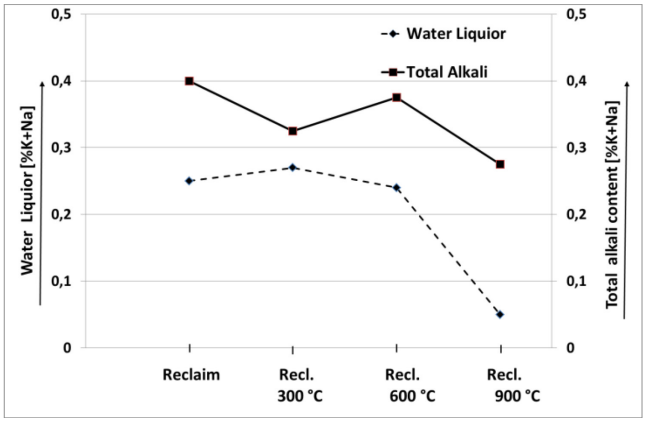


Fig. 2. Influence of annealing temperature on total and soluble alkali content

Table 4.
Alkali content in the reclaim

Sample	Water liquor		Total diss. by acids
	Na	K	Na
	%	%	%
Reclaim 300 °C	0,10	0,16	0,11
Reclaim 600 °C	0,11	0,14	0,15
Reclaim 900 °C	<0,10	<0,10	0,10
Reclaim Olivine	0,11	0,14	0,16
	Methodology – 2		Methodology – 1

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

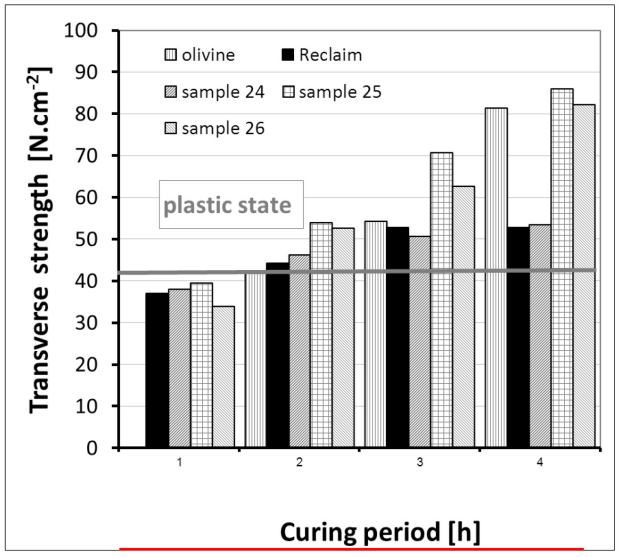
The ST –mixture corresponded to the given operating composition. Besides using the annealed reclaim (600 °C/1 h), the additive ADT – 1 (1 %) was also checked.

The reclaim wasn not deducted after annealing. The mixture with the annealed reclaim (Fig. 3) achieved even higher bending strengths than new olivine.

The addition of water to the mixture (up to 1 %) prolongs the life (bench life) of self-setting mixtures while decreasing the hardening rate and strength. While increasing the initial plastic state(Fig. 4.).

With the use of a 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.)



sample 24 reclaim 90/10 (new sand)
sample 25 reclaim 90/10 (new sand) 600° C
sample 26 reclaim 90/10 (new sand) 600° C + aditivum = Thermal Additive ADT 1

Fig. 3. Bending strengths of self-setting mixtures and influence of annealing

Fig. 4. Plastic state of self-setting mixtures in water presence (1 %) after 1 h hardening (ester HX60)

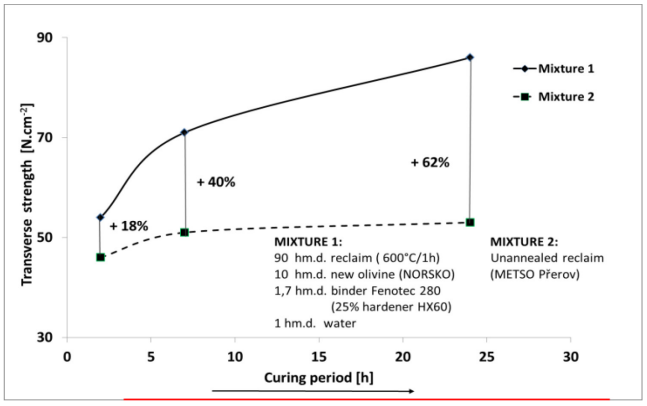


Fig. 5. Influence of the reclaim annealing on the course of bending strength of the ST – mixture

Annealing the reclaim leads to burning of the binder residues and pyrolysis products. The results are without abrasive wear and dedusting of the reclaim. A next effect can be expected including a decrease in the concentration of alkali salts .

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 electrical conductivity were determined for them (fig. 6.), and water extract alkalinity was determined using a new titration method developed by the Mining University – Ostrava University of Technology (fig. 7.).

Determination of pH: The 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 that of new olivine (pH = 9.27) but without any dependence on the kind of tested material.

Measurement of electrical conductivity: Unambiguously, the highest values were obtained for dedusted particles (3500 – 6150 μS/cm). The return mixture had considerably lower values (700 – 910 μS/cm). As expected the reclaim had even lower ones (675 – 750 μS/cm). Therefore, electrical conductivity can be considered a suitable criterion of evaluating reclaim quality.

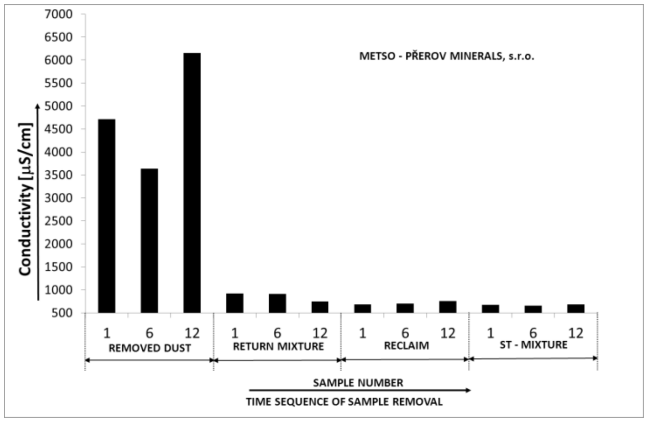


Fig. 6. Electric conductivity of chosen samples

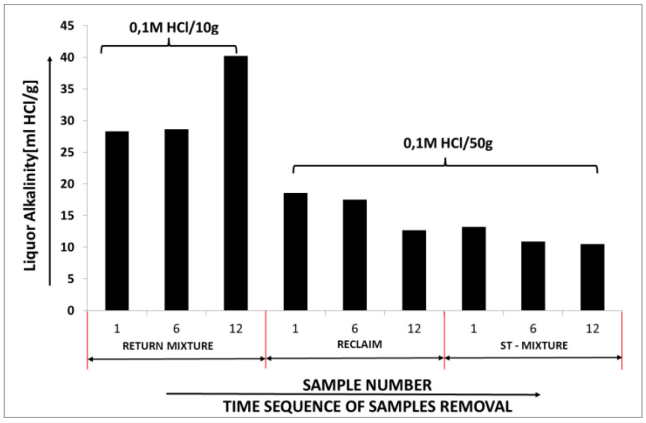


Fig. 7. Measurement of the extract alkalinity with a new process

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 a considerable portion of pyrolysis carbon and alkali (K, Na) (Fig. 9.).

Low adhesion of binder system residues forms a precondition for the high efficiency of alkalinity decrease by abrasive wear.

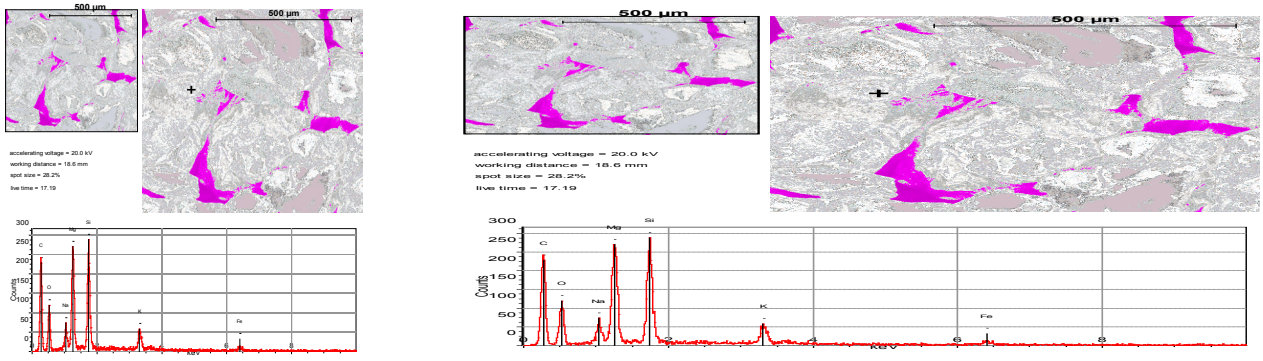


Fig. 8. Fracture surface of the self-setting mixture (90/10 new olivine; 1.7 weight parts of Fenotek 280; 22 % HX 120 for a binder, water)

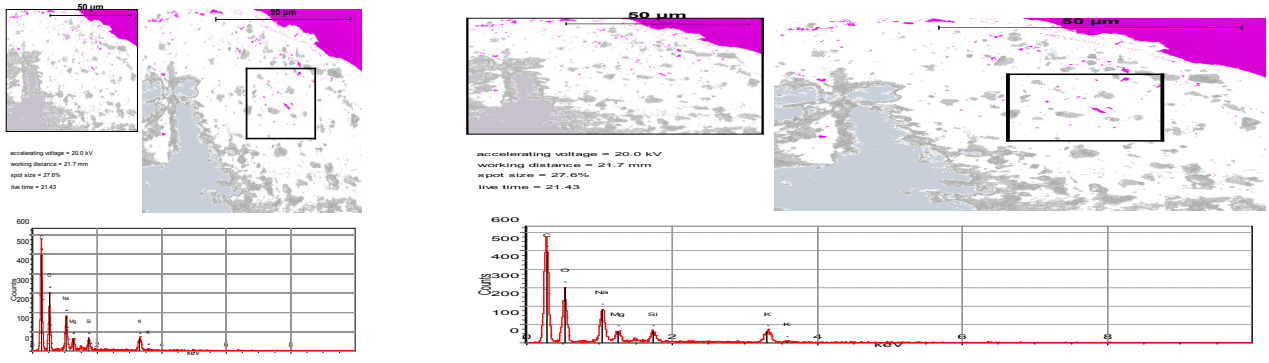


Fig. 9. A binder envelope of grains in the reclaim with high concentration of alkali salts

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 electrical conductivity of the water suspension decreases in correlation with the decrease of extractable alkali, and simultaneously the bending strength of the self-setting mixtures increased considerably (+ 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 transfers the salts into an unextractable form, making them difficult to remove.

A decrease in the concentration of alkali salts 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 electrical conductivity of the extract.

Measurements of the alkalinity of the reclaim 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.