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CHEMISTRY OF FOUNDRY SAND RESINS AND CONSEQUENCES FOR RECYCLING

The basic problem in foundry industries is the choice of an optimal binder. The binder has to meet many technical requirements, must be environmentally safe and should enable reclamation of the outcast sand.

In the paper a short review of various gas-hardening techniques has been given. Several commercial methods applied in foundry industry have been considered. The chemical mechanism as well as the possibility of reclamation of outcast sand in a given method has been discussed.

The principal problem in foundry industries today deals with the choice of an optimal binder. The binder has to be stable, it should resist the impact of a liquid metal and should break down when the metal freezes. It should also display a long shelf life, a sufficiently long bench life of the sand mixture, good shake out properties, etc. Apart from that the binder system must be environmentally safe and should promote the reclamation of the outcast sand.

The need for reclamation appears to be sharp because 90% of the core material is composed of sand. The problem has to be considered not only from ecological, but also from economical viewpoints.

It should be stressed that the sand feasibility of reclaiming is closely associated with the type of the binder system used. There will be no problem to reclaim sands bonded with clay or oil. Nevertheless, up till now it is very difficult to regenerate sands from outcasts which have been silica-bonded, which is a pity because that kind of binder gives no rise to environmental discomfort.

Actually there exist two general methods to reclaiming the outcast sands. Both are attrition- and impact-based. The first method works in wet condition and is suitable for silica-bonded sands, the other is a dry method. Only the dry method appears to be economically inacceptable since every drying operation is expensive. Chemical reclamation is also too costly and cumbersome.

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A classification of main technologies for manufacturing mould and core materials is outlined in table 1.

Table 1

Basic processes for core and mould manufacturing

	Hot box	Warm box	No bake	
			Self set	Gas hardened
Temperature, °C	≥ 250 °C	150–180 °C	ambient	ambient < 150 °C
Type of sand binder	FA; FA/F; FA/Ph/F	U/FA/F (≥ 70% FA)	FA; FA/F (50–90% FA); rare U/FA/F	Various (see table 2))
Hardner or catalyst	H_3PO_4; organic sulfonic acids; NH_4Cl	Cu salts of organic acids	H_3PO_4 (20–60% of binder weight); H_2SO_4	CO_2; SO_2 (peroxide; tertiary amines, methyl formate; warm air)
Time needed for curing	seconds	minutes	hours	

FA – furfuryl alcohol; F – formaldehyde; Ph – phenol; U – urea.

The critical issue in foundries today is gas hardening coupled with reclamation of sand. Different gases are used for that purpose (table 2).

Table 2

Schedule of gas-hardening systems

Binder type	Gas	System name
Phenolic uretane resin	Organic amines	Isocure, Cold-box Plus
Furan resin	SO_2	Sapic, Hardox, So-Fast, Insta-draw I
Epoxy resin	SO_2	Epoxy Insta-draw, Rütapox
Modified urethane resin	SO_2	FRC/Isoset
Phenolic resin	Methyl formate	Betaset
Sodium silicate	CO_2	CO_2 process
Sodium silicate	Air	Warm-air process
Polyacrylate resin	CO_2	Polidox
Polyacrylate resin	Air	Arbond

It has been proved that the choice of resinous material is wide. Only in the United States, 25 thousand tonnes of furfuryl alcohol are utilized in foundries for sand-bonding annually. Furfuryl alcohol co-reacts easily with other monomers like formaldehyde, urea, phenol, etc. The hardening process proceeds in an acidic medium only, which is attainable in different ways giving rise either to self-setting or to gas-hardening systems (table 1, figure 1).

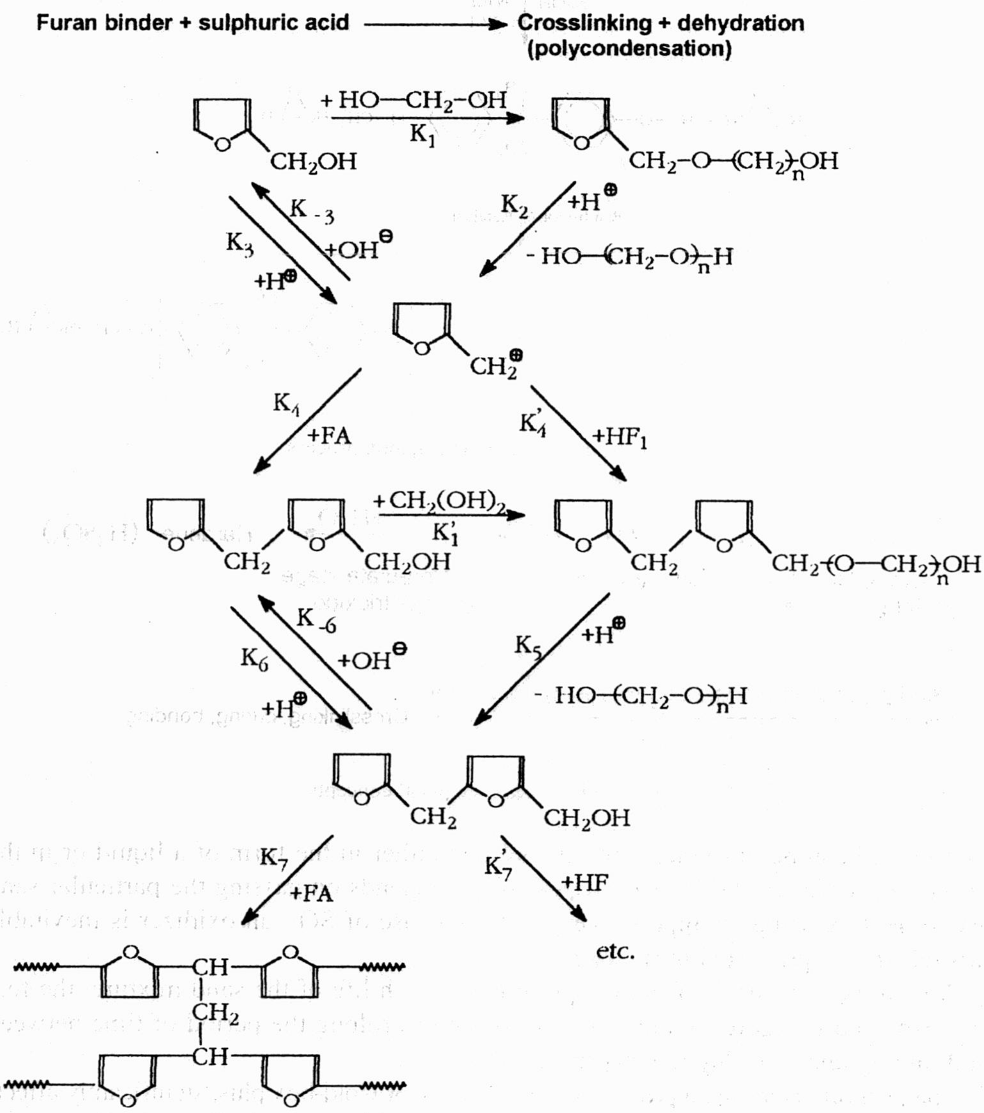


Fig. 1. Hardox process

Epoxy resins are very often substituted for furan resins. Such a system consists of two components: a linear difunctional reactant and multifunctional crosslinker. Both have glicydyl end-groups (figure 2, table 3), and also need an acid for hardening.

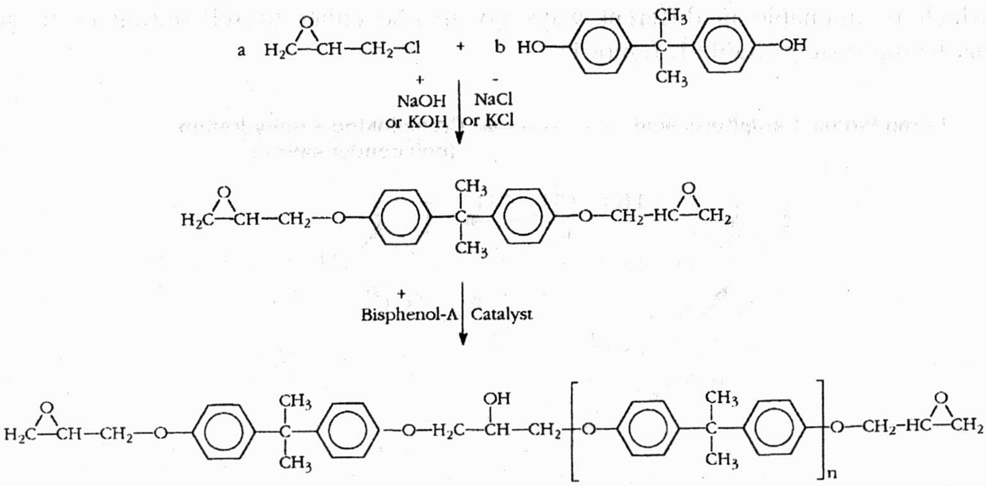


Fig. 2. Epoxy resins in the Rütapox process

$$SO_2 + 1/2\,O_2 \longrightarrow SO_3 \xrightarrow{+H_2O} \text{Hardener } (H_2SO_4)$$

Gassing agent, sulphur dioxide — (from peroxide) — Intermediate stage, sulphur trioxide

Binder (furan or modified epoxy resin) + hardener ⟶ Crosslinking, curing, bonding

Fig. 3. SO_2 process, chemical concepts

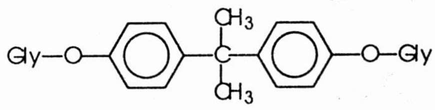
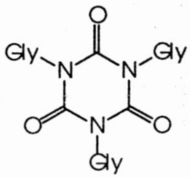
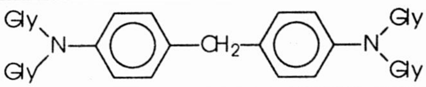
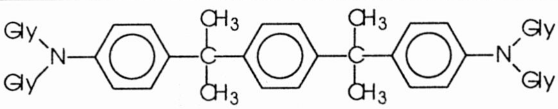
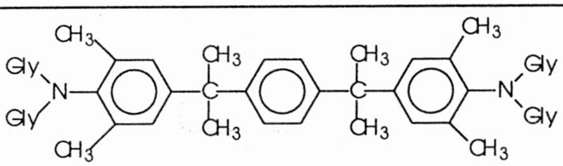
The acid can be introduced into the system either in the form of a liquid or in the form of a powder (NH_4Cl). A third possibility depends on gassing the particular sand mix in the box using an appropriate gas. In the case of SO_2, an oxidizer is inevitable (this reaction is presented in figure 3).

A great benefit results from the prolonged bench life of the sand mixture, the feature displayed in figures 4 and 5. It is possible to prolong the period of time between sand mixing and inserting the mixture into the box.

The phenolic-isocyanate process, termed Isocure or Cold-box plus, significantly affects the productivity. The chemistry of this process is roughly shown in figure 6. The components are mixed in equivalent amounts and subsequently introduced into sand which must be dry. Contrary to SO_2, the tertiary amine catalyses the process, but it is not an integral reactant. Methyl formate used for the Betaset process is, contrary to isocyanates, not sensitive to water. It is a very volatile compound and boils at 32 °C. Due to the condensation reaction presented in figure 7 the alkali catalysed resin hardening.

Table 3

Selected structures of epoxy resins

Structure	Functionality and name
	Difunctional, DGBA
	Trifunctional, TGIC
	Tetrafunctional, TGGDM
	Tetrafunctional, TGBAP
	Tetrafunctional, TGMBAP

Gly = glycidyl (epoxy) group; DGEBA = diglycidylether of bisphenol-A; TGIC = trigycidyl isocyanurate; TGDDM = N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenylmethane; TGBAP = N,N,N',N'-tetraglycidyl-α,α'-bis(aminophenyl)-*p*-di-isopropylbenzene; TGMBAP = N,N,N',N'-tetraglycidyl-α,α'-bis(3,5-dimethyl-4-aminophenyl)-*p*-di-isopropylbenzene.

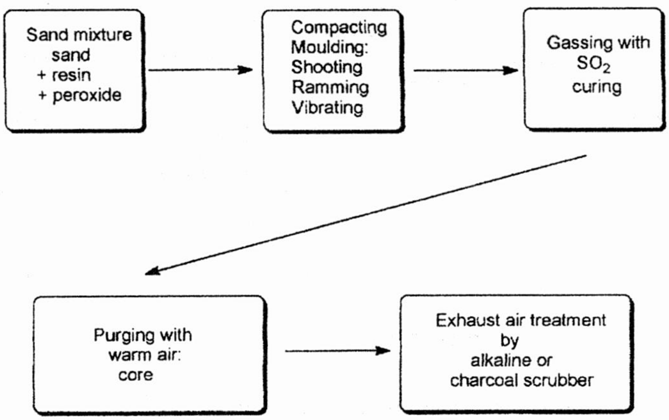


Fig. 4. Hardox and Rütapox processes

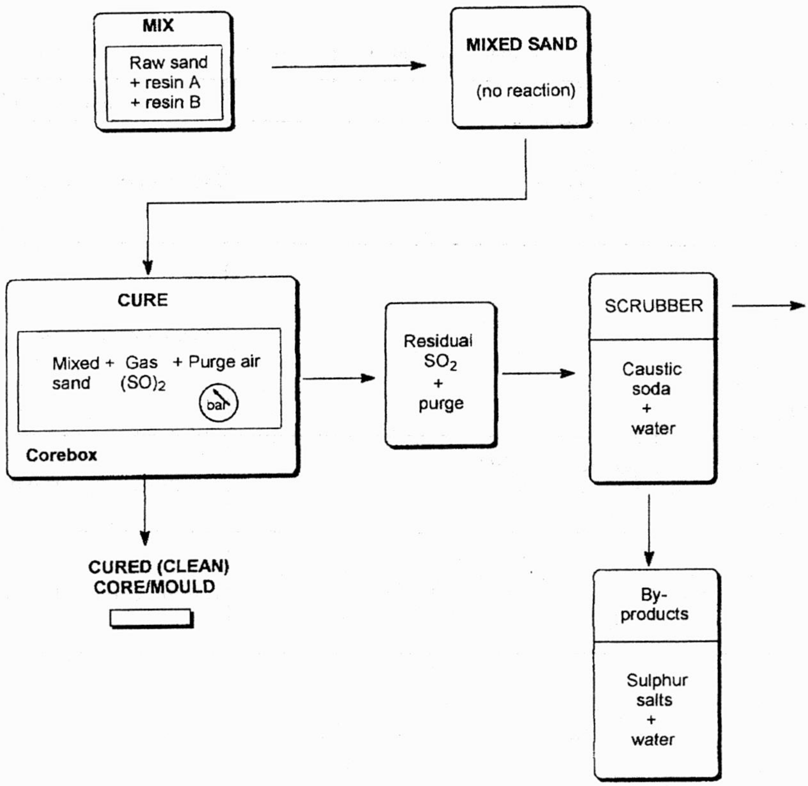


Fig. 5. Operation of epoxy SO_2 system

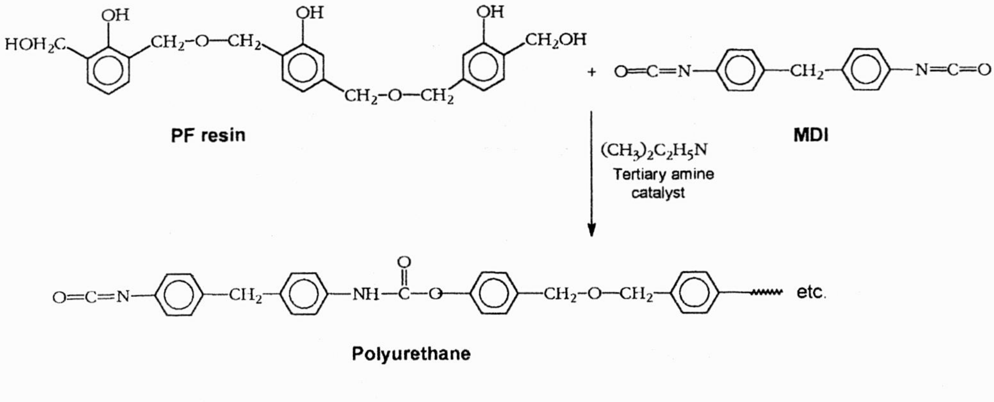


Fig. 6. Schematic representation of reaction occurring during the Isocure or Cold-box process

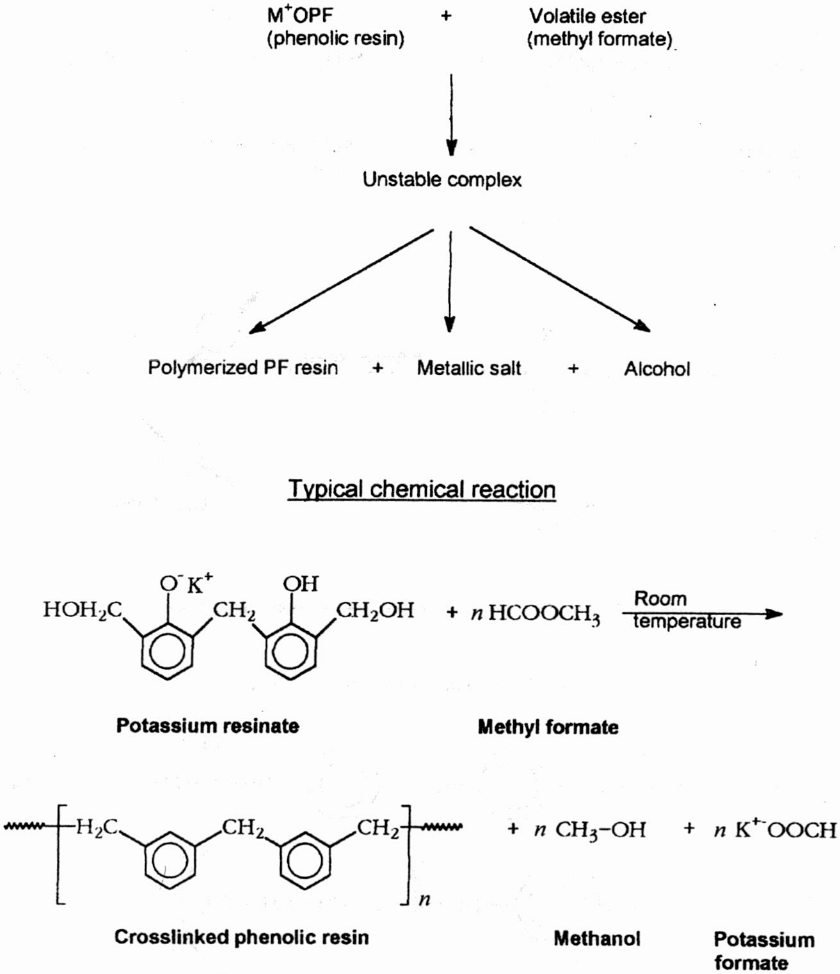


Fig.7. Schematic representation of the reaction mechanism of the Betaset process

The ester process has replaced many other technologies used in former years. Environmentally safe is the Free Radical Cure (FRC) process which utilizes a two-component resin made of urethane-based substrates having C=C double bonds as end groups. The reaction scheme and the possible substrates are outlined in figures 8 and 9.

The cores and moulds thus obtained display excellent storage properties and no humidity absorption is observed. In the FRC process, the consumption of SO_2 is 10 times lower compared to the Hardox process. Adhesion promoters are also added to the sand. Quick hardening and high dimensional accuracy are considered to be further advantages associated with that process.

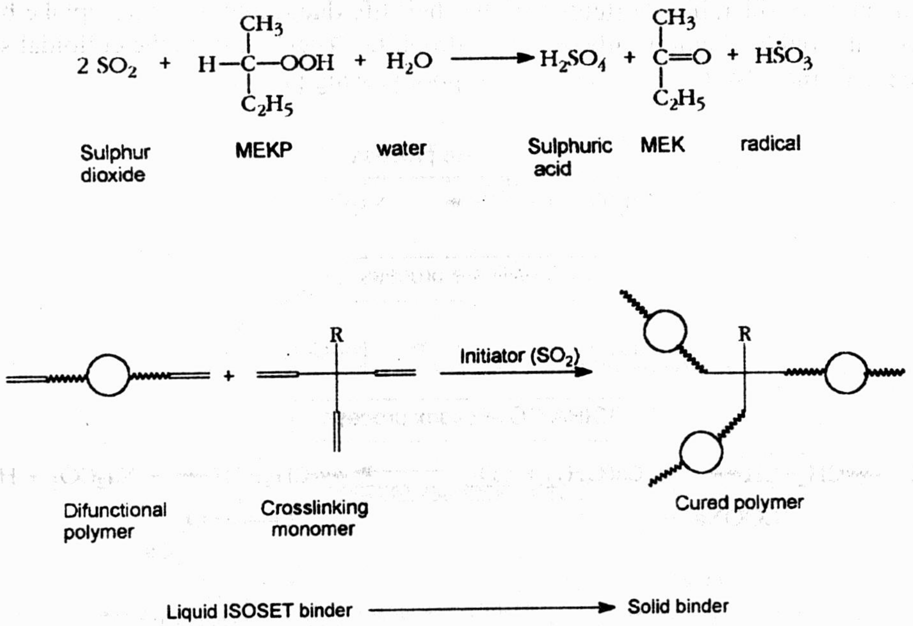


Fig. 8. Mechanism of Free Radical Cure

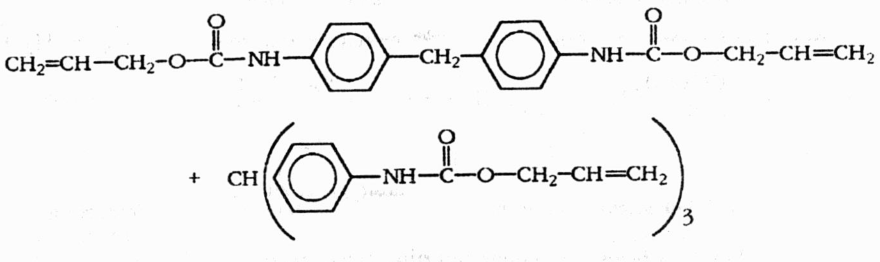


Fig. 9. Difunctional and crosslinking monomers
in potential sand-binders in the Isoset process

Silicate-based binders are regarded to be environmentally safe. It was one of the main reasons why the CO_2–silicate process (figure 10) has dominated the field of foundry binders for more than 20 years, i.e. since the seventies. However, two drawbacks inherent in that technology have not been eliminated up till now. The main disadvantages are: bad knock-out properties and the impossibility of accomplishing an economically feasible reclamation of the outcasted sand.

Principally the reclamation of silica-bonded sand is possible, but only if the wet-attrition method is used. Since drying is indispensable, this method has proved too expensive. Application of dry attrition methods in the case of silica-bonded sands results in a considerable shortening of the shelf life due to the moisture uptake by the cores and moulds. Sodium carbonate is hydrophilic. Together with the colloidal silica, which is formed, Na_2CO_3 give also rise to poor gassing properties.

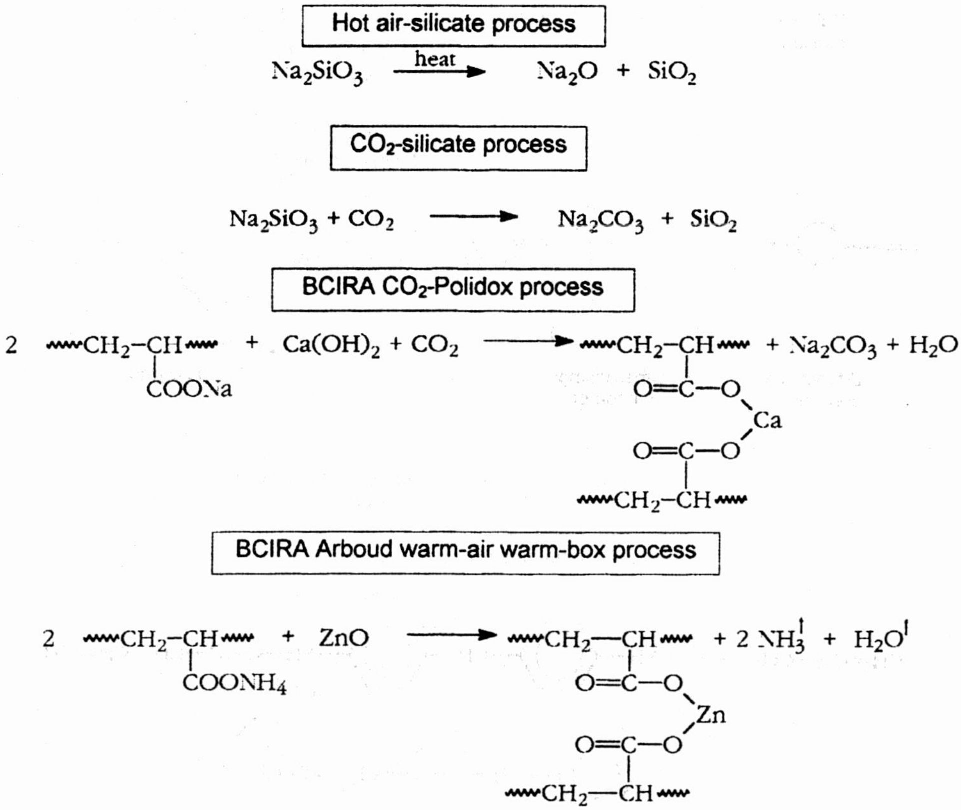


Fig. 10. Chemical reactions occurring in the processes indicated

There have been attempts to solve this problem by applying a high-speed hammer mill (2000 rev/min), but they failed. As mentioned earlier, the problem of reclamation is acute because the foundry materials are composed of more than 90% of sand. The sequence of operations involved in a reclamation procedure is highlighted in figure 11. The key part of the procedure is most often the pneumatic set which is shown in figure 12.

Due to very stringent laws established in Sweden in order to protect environment, two new prospective binder systems have been developed. Both methods are based on poly(acrylic acid). The first is known as the Brick Polidox Process, while the other is termed Bcira Arboud warm-air warm-box process. In the latter, the temperatures applied range from 100 to 150 °C.

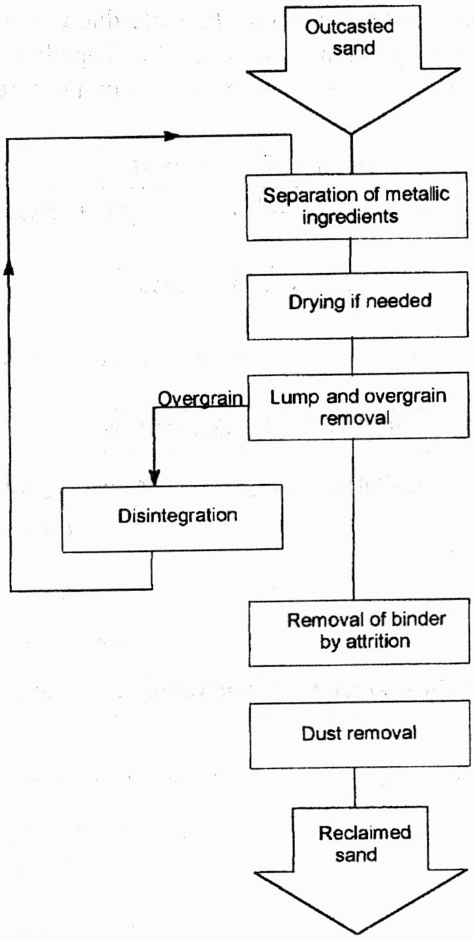


Fig. 11. Schedule of operations in sand reclamation

In the Polidox process, the sand is mixed with an aqueous solution of sodium polyacrylate followed by the addition of calcium hydroxide in the form of powder (figure 10). After compacting the mixture in the box, the gassing with CO_2 is started which causes the hardening of mould or core at ambient temperature. The needed amount of CO_2 is up to 1% by weight of sand. The bench life, however, is relatively short, and the flow ability is also poor. Nevertheless, this process can successfully replace many other processes and is an alternative to hot-box and cold setting procedures.

The Arboud process should be regarded as a step forward in the development of more and more effective sand binders. Ammonium polyacrylate and powdered zinc oxide are used as components (figure 10). Resin addition is at the 2% level and the curing temperature ranges between 100 and 150 °C.

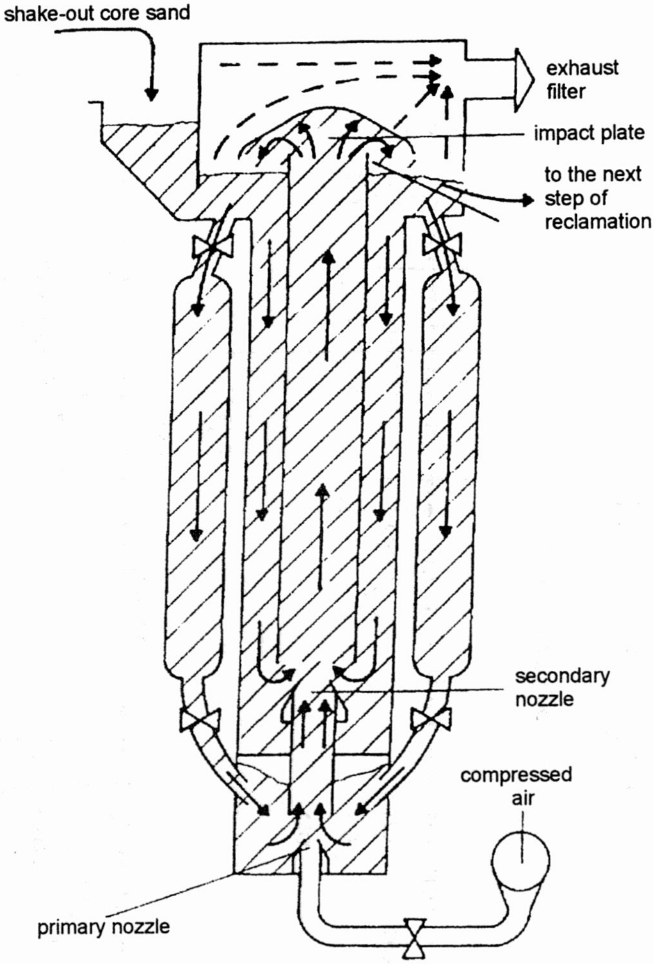
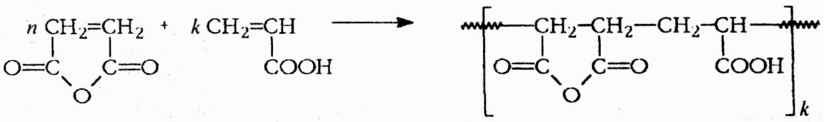


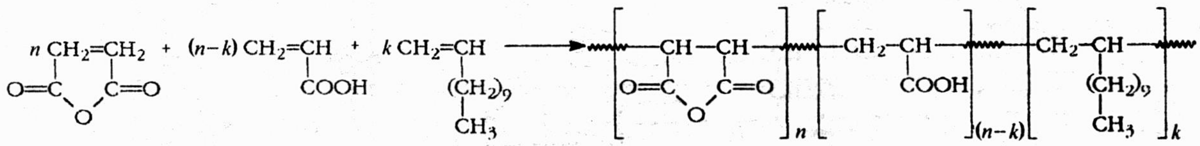
Fig. 12. Reclamation of core sand by pneumatic treatment

In our laboratories, various water-soluble polymers have been developed which appeared to be suitable for sand-bonding after the addition of proper metallic compounds for cross-linking. Apart from that we also try to replace glutaric aldehyde with formaldehyde. The most important copolymers are outlined in figure 13.

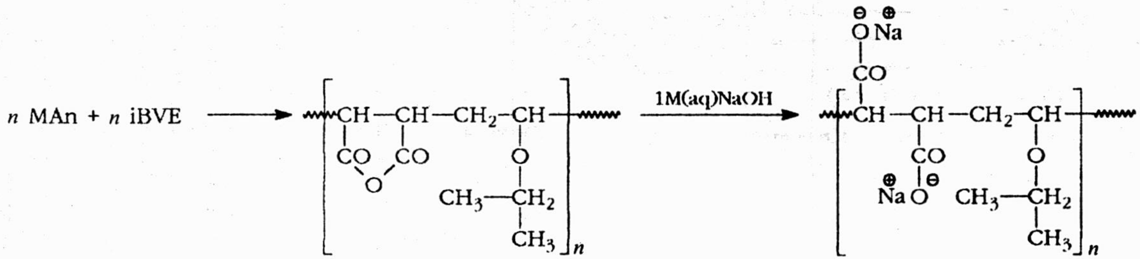
In order to make the binders less sensitive to air humidity, small amounts of α-olefins have been incorporated into the hydrophilic chains, which allows the water-soluble polymers to acquire amphiphilic properties. Besides zinc oxide we also try to apply aluminium and calcium compounds as hardeners.



MAn **AA** **poly(MAn-co-AA)**



MAn **AA** **DD**



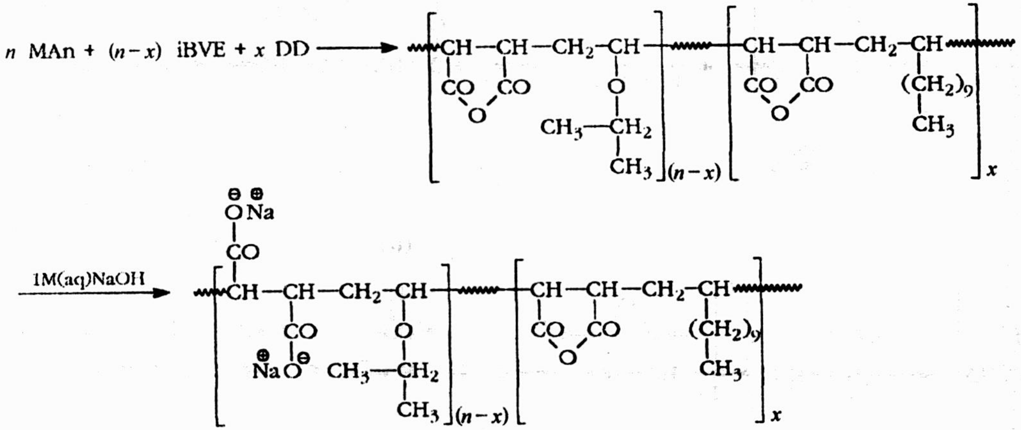


Fig. 13. Potential copolymers for sand binding
Designations: Man – maleic anhydride; AA – acrylic acid; iBVE – isobutyl vinyl ether; DD – dodecane

CHEMIA I RECYKLING ŻYWICZNYCH MAS FORMIERSKICH

Jednym z podstawowych problemów w przemyśle odlewniczym jest wybór odpowiedniego spoiwa. Właściwie dobrane spoiwo powinno odpowiadać normom technicznym, nie stanowić zagrożenia dla środowiska i jednocześnie umożliwiać recykling zużytych mas formierskich.

W artykule przedstawiono krótki przegląd technik utwardzania z wykorzystaniem różnych gazów. Rozważono kilka praktycznie stosowanych w przemyśle odlewniczym metod. Omówiono chemiczne mechanizmy oraz możliwość regeneracji zużytych mas formierskich w poszczególnych procesach.