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Advances in Technology of Soluble Cores for Die Castings

P. Jelínek, E. Adámková*, F. Mikšovský, J. Beňo

Department of Metallurgy and Foundry, VŠB – Technical University of Ostrava,
17. listopadu 15/2172, 708 33 Ostrava-Poruba, Czech Republic

*Corresponding author. E-mail address: eliska.adamkova@vsb.cz

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Abstract

A number of technologies is developed that substitute simple metal cores in the high-pressure casting technology. Soluble cores, namely on the salt basis, represent the highest prospect. The contribution gives the results of the production of salt cores by high-pressure squeezing and shooting with using a binder. Special attention is paid to the shape of NaCl salt crystals with additives and the influence on strength properties of cores. A technology of bonding the salt cores is developing. Salinity of circulating water is studied and it is checked with the aid of electrical conductance.

Keywords: Salt cores, Manufacture by squeezing and shooting, The use of cooking salts, Bonding of cores, Salinity of cleaning water, Electric conductance

1. Introduction

The rising demands on the complexity of castings cannot be met in the die casting technology with the existing simple metal cores. Therefore the interest in new manufacturing processes of “soluble” cores (Verlorene Kerne, Lost Cores) is growing [1]. The greatest potential represent the cores of inorganic salts which must meet a number of requirements as follow:

- Dimensional accuracy
- Bench life (hydration)
- Strength even at increased temperatures (up to 700 °C)
- Smoothness of precast cavities (Ra)
- Ease solubility in water

According to some authors the salt cores are suitable for lower rates of filling the mould (under 35 m/s) with limited post pressing, i.e. suitable e.g. for the rheocasting technology [2]. The contribution deals with the development of salt cores by the

method of high-pressure squeezing of crystalline salts and shooting with the use of binders (alkali silicates), the application of cooking salts of different provenance, gluing of cores and with recycling the brine.

2. New manufacturing processes of “soluble” cores

- Sand cores – made by the technology of PUR Cold – Box (binder – polyurethanes) [3] or Warm – Box (alkaline silicates). Precast holes are geometrically precise but the cores are removable with difficulties (in case of organic binders by annealing which is often recommended to be performed simultaneously with heat treatment of castings of some Al-alloys) [4]. Metal penetration can be avoid by optimization of base sands granulometry and with the aid of protective coatings. Sometimes it is proposed to dip the cores in binders (resin, water glass).

- Cores of the plastics (polyoxymethylene) – are made by machining the blocks. They are removed by combustion of cores residues.
- Cores of low melting metals, e.g. Zn-alloys (ZnAl4CU1) [2]. They are melted out by additional annealing of castings. The surface of holes is of high quality corresponding to the die casting process.
- Cores of inorganic salts:
 - Hollow cores combined with a metal pipe [5][6][7].
 - Full cores of crystalline salts or their melts [8].

The use of salt cores is already a longer time known with gravity or low-pressure casting processes (pistons of internal combustion engines) but for demanding high-pressure casting an intensive research is only realized [6, 8, 9, 10, 11, 12, 13, 14] in spite of a fact that the beginnings go back to the 70th-80th years of the last century [15] [16].

3. Salt cores

They are developed basically in the manufacturing technology of salt cores. Each of them has its merits and shortcomings (tab. 1.).

Table 1.
Advantages and disadvantages of technologies for preparation of cores

	High-pressure squeezing	Shooting (binder alkali silicate)	Casting of molten salts with post pressing
Advantages	<ul style="list-style-type: none"> - High cold and hot strength - Minimum porosity (2 – 6 %) - Simple manufacturing process - No protection against penetration is needed - Cores can be machined - Accuracy of precast holes - Good solubility in water - High resistance to rehydration 	<ul style="list-style-type: none"> - Possibility of using the existing core machines - Manufacture of complex shapes - Excellent solubility in water 	<ul style="list-style-type: none"> - High cold and hot strengths - Minimum surface porosity - No surface protection is necessary - High accuracy and smoothness of precast holes
Disadvantages	<ul style="list-style-type: none"> - Designed for simpler shapes - Non-uniform degree of compaction (one-way pressing) 	<ul style="list-style-type: none"> - Lower strengths - Higher hygroscopicity of cores - High porosity (30 – 35 %) - Worse surface quality (protective coatings) 	<ul style="list-style-type: none"> - Expensive special equipment and demanding preparation - Volume shrinkage during solidification - More difficult solubility (high water consumption) - High energy consumption

3.1. Salt cores manufactured by squeezing

Our first experiments resulted from KCl and NaCl of chemical purity (p.a.). Although the physico-chemical properties of both salts don't differ substantially, the KCl in all parameters shows significantly higher cold and hot strengths (up to 650 °C) (tab. 2.) which is explained at first by different angularity and shape of grains [17] which is also confirmed by C. R. Loper [16] too.

Table 2.
Bending strength of pressed cores (100 kN, 56 MPa)

	Holding in air 48 h [MPa]	Hot 650 °C [MPa]	Residual strength 650 °C/1 h [MPa]
KCl, p.a. ⁺⁾	7.53	> 8.9	8.49
NaCl, p.a. ⁺⁾	3.63	5.33	2.55
Angularity of salt grains:	KCl ⁽⁺⁾ = SPHT 3		0.778
	NaCl ⁽⁺⁾ = SPHT 3		0.906

Further growth of cold and hot strength was achieved by applying of **composite salts** resulting from an assumption that the additives of the ZrSiO₄, Al₂O₃, Fe₂O₃ a SiO₂ type of defined

concentration and granulometry will interfere the long dislocation lines with particles of high heat resistance dispersed in the salt matrix (KCl, NaCl). Composite salts have brought as follows:

- The growth of cold and hot strengths (650 °C) and namely the highest one with the α -Al₂O₃ additive. Primary bending strength exceeded 9 MPa which is approximately a triple of strength of the PUR Cold – Box cores [3].
- Residual strengths after the exposure of cores to 650 °C/1 h were by 10-20 % higher than primary strengths.
- With the growth of pressing forces (up to 200 kN) the porosity of cores was decreasing under 6 % (the cores are of a glassy, monolithic character), their strength is growing but the smoothness of precast holes too (Ra < 5 μm). Mean diameter of pores kept around 0.0618 μm.
- Cores can be mechanically machined.
- With strengths of cores the high kinetics of dissolving in water doesn't decrease (20 °C).

Spontaneous destructions of cores caused by residual stress after high-pressure squeezing can be prevented by special thermal treatment and modifications of the pressing element. Contrary and volume pressing are tested (3D).

3.2. Salt cores manufactured by shooting

They require the use of binders hardenable with the heat of core boxes or cold hardenable, e.g. with a gaseous medium (TEA – PUR Cold – Box). Our research was focused on environmental friendly inorganic binders (Na – silicates) [18] made by a direct production ($M < 2.1$) hardened by a dehydration process, the Warm – Box technology (up to 250 °C). After shooting the mixture the cores are hardened in a hot core box (7.5 – 8.0 bar, 190 °C). The achieved real porosity of cores ranged in the interval of 21.3 – 23.5 % (apparent porosity of 35 – 45 %) which correlated with bending strength of 1.5 – 3.5 MPa. It is ca $\frac{1}{3}$ - $\frac{1}{2}$ of strength of cores squeezed from the mixture of the same composition. In this case the metal penetration must be avoided by a surface protection with the aid of alcohol-based protective coatings. Otherwise during storing this cores are also exposed to higher rehydration (fig. 1.).

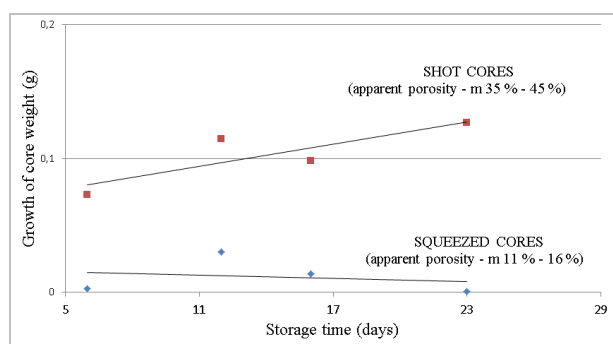


Fig. 1. Comparison of hygroscopicity of squeezed and shot cores of the same composition (conditions RH 35 – 58 %, T = 20.7 – 24.9 °C)

Table 3.

Chemical composition of chosen cooking salts

Salt sample	Trade name	Additives	Presence of compounds
1	Edible rock salt with iodine and fluorine (finely ground)	F	NaF
		I	27±7 mg/kg KIO ₃
2	Edible rock salt with iodine (finely ground)	I	20-35 mg/kg KI KIO ₃
3	Alpine salt with iodine (vacuum treated)	NaCl	98.8 %
		CaCO ₃	min. 0.9 %
		MgCO ₃	min. 0.2 %
		KIO ₃	33-58 mg/kg
		I	20-34 mg/kg KIO ₃
4	Alpine salt with fluorine and iodine (vacuum treated)	NaCl	98.0 %
		CaCO ₃	min. 0.7 %
		MgCO ₃	min. 0.1 %
		KIO ₃	33-58 mg/kg
		I	20-34 mg/kg NaF
5	Fine sea salt with iodine (evaporated from sea water)	F	max. 250 mg/kg
		I	15-35 mg/kg KIO ₃
6 Standard	NaCl, p.a. (chemically pure)	Fe	max. 0.0003
		Heavy metals (Pb)	max. 0.0005 %
		SO ₄	max. 0.005 %
		Ca	max. 0.005 %
		Mg	max. 0.002 %
		I	max. 0.008 %
		Br	max. 0.01 %

In case of short-term storage the growth of weight is insignificant. During solution in water the cores behave in a similar way.

4. Application of cooking salt of different provenance for cores

Five types of cooking salts (No 1÷5) were chosen from the commercial offer and they were compared with a standard of NaCl, p.a. (No 6). Chemical composition (tab. 3.) can be evaluated from two points of view as follow:

- Health point of view
- Technological point of view

From the point of view of health the cooking salts contain health useful elements, iodine and fluorine, and namely in a form of compounds (KIO₃, KI, NaF) in amounts 15 – 58 (max. 205) mg/kg. But for manufacture of salt cores the technological points of view are much more important, the parameters limiting their quality. In some salt kinds the additives preventing the grain sticking, so called „anticaking agents“ are found. For this purpose the K₂CO₃, CaCO₃, MgCO₃, SiO₂, K₄[Fe(CN)₆].3H₂O additives are used. Especially the occurrence of carbonates is characteristic for Alpine salts. Anticaking additives adversely influence the manufacturing technology of salt cores, and namely both the high-pressure squeezing and the shooting too. Gluing – binding properties are deteriorating (fig. 2.) and namely both by the recrystallization way (squeezing) and by binding between the salt grains and alkali silicate (shooting) too.

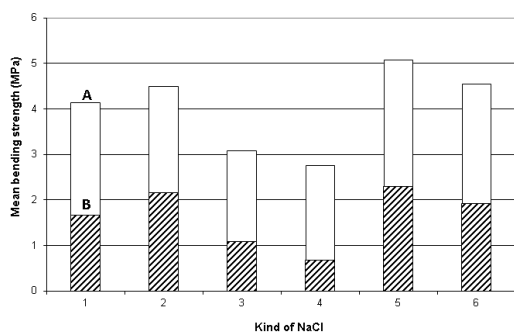


Fig. 2. Comparison of strengths of salt cores squeezed and shot from different kinds of cooking salts (mean value from 6 cores; the fraction $0.063 \div 1.0$ mm; A = SQUEEZED CORES (104 MPa); B = SHOT CORES (the binder Na – SODIUM SILICATE, 7.5-8.0 bar)

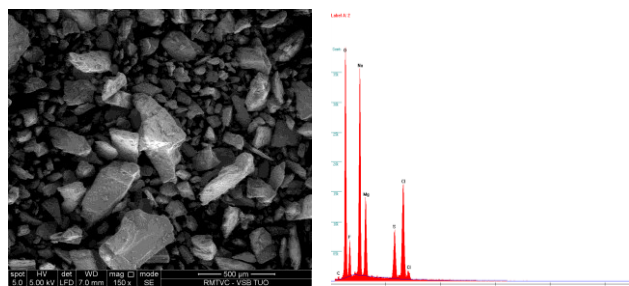


Fig. 3. Shattered surface of crushed rock salts (samples Nos 1, 2) and EDX analysis of chemical composition

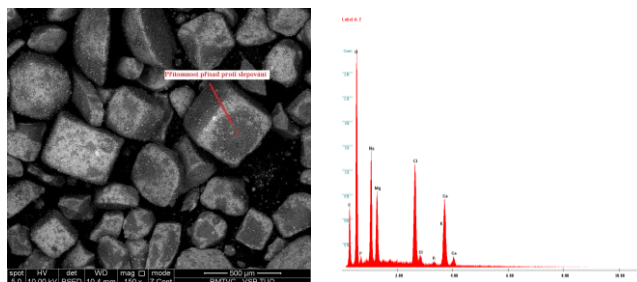


Fig. 4. Regular cubic grains of Alpine salts (samples Nos 3, 4) and EDX analysis confirming the presence of anticaking additives on the salt grain surface ($MgCO_3$, $CaCO_3$)

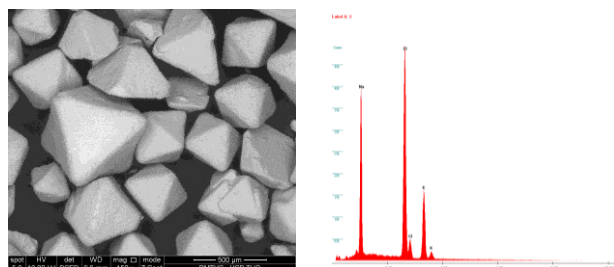


Fig. 5. Dipyramidal regular shape of NaCl, p.a. – standard (sample No 6) and EDX analysis of chemical composition

In general, by squeezing the significantly higher strengths were achieved for all kinds of salts. The lowest strengths had the cores with cubic regular shape of grains („Alpine salt, Nos 3, 4 – recrystallized salts) (fig. 4.), while the highest strengths were achieved for crushed rock salts (Nos 1, 2) (fig. 3.) and sea salt (No 5). But this is not valid for the standard (NaCl, p.a., No 6). A „dipyramidal, regular“ shape of grains gives high strengths both of squeezed and shot cores. This shape is closest to the globular shape of the quartz base sand what is an advantage both for shooting and squeezing (fig. 5.).

5. Gluing of salt cores

In case of precast holes of complex shapes in castings the necessity of gluing the cores (salt – salt, salt – metal) can be assumed. Besides achieving the necessary strength of the bond even under elevated temperatures it is important to achieve the dimensional accuracy (to ensure the thickness of bonding) and to remove the glued joint during dissolving the salt cores. For this purpose 4 kinds of industrially produced glues and one own research product (VŠB – TUO) were proposed (tab. 4.).

Table 4.

Strength of core joints (shear strength) salt – salt

Glue	Glued surface [cm ²]	Strength of the sample [N/cm ²]	Shear strength [N/cm ²]
FZ 50C			
Heat resistant glue for gluing of chamotte bricks	9.8	25	63
Górkal 50C			
Heat resistant glue – cement for manufacture of concrete of fire-resistant celluloses Usable up to 1700 °C	10.4	40	96
H 2400 Usable up to 1060 °C	10.4	43	103
H 1000 Usable up to 760 °C	10.4	44	105
VŠB – TUO			
A glue based on alkali silicates	10.4	34	67
		38	81

Shear strength of the core joints salt – salt ranged within 63 – 105 N/cm² and salt – metal within 160 – 232 N/cm² (tab. 5).

Table 5.

Strength of core joints (shear strength) metal – salt

Glue	Shear strength [N/cm ²]
Górkal 70	216
	226
	232
VŠB – TUO	165
	183
	170
H 1000	167
	160
	164

Strength can be further on increased by thermal treatment or by combining the glues, e.g. Górkal 70 and alkali silicate ($M = 1.84$).

As shown by the casting tests the achieved strengths are sufficient even under elevated temperatures during casting ($700\text{ }^{\circ}\text{C}$). Differences of individual glues have not been proved until the cores were dissolved. While the glue H 2400 during dissolution of cores in water remained quite maintained (fig. 6.), the adhesive of VŠB – TUO was dissolved (fig. 7.). The tests have shown that gluing of salt cores even in combination with metal is real. Further development is focused on dimensional accuracy of glued cores and the use of protective coatings for “covering” the glued joints.



Fig. 6. H 2400 during dissolution of the glued core



Fig. 7. Test with the VŠB – TUO glue during dissolution of the glued core

6. Checking the state of concentration of salts in circulating wash water (kinetics of dissolution of cores, changes in electric conductance and pH of the system)

For measuring the state of salt concentration in the waste brine the signalling of the change of **pH** and **electric conductance** of the system was used. The measurement was carried out on cylindrical shot cores of chemical composition: NaCl, cooking salt + NaCl dust + graphite + water glass. It was dissolved in water under temperature of $19.5 \div 20.0\text{ }^{\circ}\text{C}$ and different NaCl concentration in wash water (standard – pure water; the amounts of 145 g and 240 g NaCl in water). The

measurement was based on a consideration that during removing the cores with already used water the solubility will decrease (the growth of the brine concentration) which is also confirmed with results given below (fig. 8.).

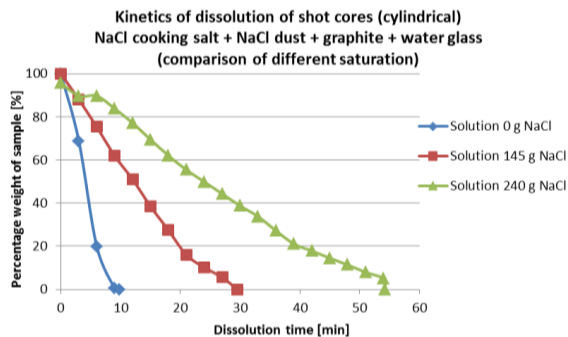


Fig. 8. Comparison of dissolving the salt cores in two types of saturated solutions and in pure water

While in case of pure water the sample was dissolved for 9 minutes, with 145 g of NaCl present in the solution it was already 30 minutes and with amount of 240 g of NaCl the sample was dissolved for 54 minutes.

Fig. 9. shows a significant growth of electric conductance with the loss of weight of the salt core (growth of concentration of NaCl in pure water). On the contrary the pH value of the system increased from a neutral level to alkaline values (pH around 9) for a short time and with further enrichment of salts in water it wasn't further changed.

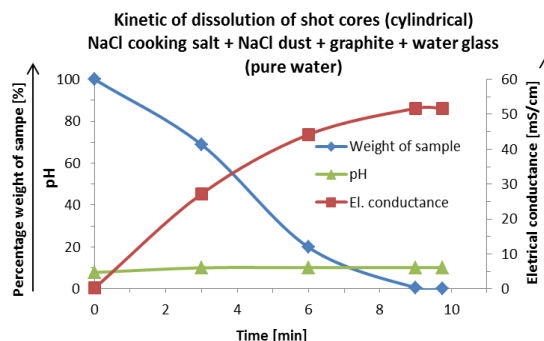


Fig. 9. Kinetics of dissolution of salt cores in dependence on pH and electric conductance

It turns out that the best criterion for the evaluation of reversal usability of wash water is **electric conductance**. Therefore for a specific chemical composition of the salt core a critical value of electric conductance can be determined which still allows the effective solubility of cores of the given composition. The methodology has a task to indicate a critical concentration of the brine still applicable in the closed circuit of wash water.

7. Conclusion

Salt water soluble cores offer a considerable potential even for so demanding manufacturing technology of castings as is high-pressure casting process. For developed methods of squeezing and shooting of cores with use of inorganic binders of composite composition a significant influence of granulometry and the shape of grains was proved but above all the unwanted presence of „anticaking“ additives in cooking salts. A way of gluing the salts cores and the combination with metal cores too is studied. The attention was paid to the kinetics of dissolving the cores and to study of critical salinity of circuit water during cleaning of castings.

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