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WATER-SOLUBLE CORES – VERIFYING DEVELOPMENT TRENDS

JEDRA, TOPNA V VODI – PREVERJANJE SMERI RAZVOJA

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Application of pure inorganic salt-based cores has been known since the end of the 20th century, especially in the field of gravity and low-pressure die casting. The contemporary trend in technology leads to the use of the cores in the field of non-ferrous-alloy high-pressure die casting. The main methods of the core production include high-pressure squeezing and shooting (warm core box). During research processes it was shown that pure-salt application is not very suitable for high-pressure casting. That is why a composite salt-based matrix of defined properties was started to be used. The aim of the paper is to verify the influences of the chemical composition, shape and morphology of the grains of various NaCl compounds on the mechanical properties (the bending strength) of water-soluble salt cores used for Al-alloy high-pressure die casting and to evaluate their properties resulting from the squeezing and shooting methods.

Keywords: salt cores, inorganic salts, die casting, warm box, non-ferrous metals

Uporaba jeder iz čistih anorganskih soli je poznana že od konca 20. stoletja, še posebno na področju gravitacijskega in nizkotlačnega litja. Podobne usmeritve in tehnologije vodijo k uporabi jeder na področju visokotlačnega litja neželeznih zlitin. Med glavnimi metodami izdelave jeder sta visokotlačno iztiskanje in vbrizganje (segreti jedrnik). Raziskava je pokazala, da uporaba čiste soli ni najbolj primerna za visokotlačno litje. To je razlog za začetek uporabe kompozitnih jeder na osnovi soli. Namen članka je preveriti vpliv kemijske sestave, oblike in morfologije zrn različnih vrst NaCl na mehanske lastnosti (upogibna trdnost) in uporabnost v vodi topnih jeder za visokotlačno litje Al-zlitin ter oceniti njihove lastnosti po stiskanju ali vbrizgavanju.

Ključne besede: jedra iz soli, anorganske soli, tlačno litje, segret jedrnik, neželezne kovine

1 INTRODUCTION

Together with the development in various technical fields (the automotive industry) the demand for more and more difficult and challenging castings increases; these are mechanically cleanable only with large difficulties. The application of the technology of disposable, inorganic, water-soluble salt cores is one of the solutions for the difficulty of a core removal from the areas that are hardly accessible for mechanical cleaning.[1] A reverse crystallization of the salt from a water solution is enabled due to the core water solubility, which is a requirement for creating an environmentally friendly closed circuit of the core production.

The usage of water-soluble salt cores has been so far known in the field of non-ferrous-alloy gravity and low-pressure die casting.[2] Promising possibilities can be created by focusing the investigation on the development of water-soluble salt-core application technology in the field of Al-alloy high-pressure die casting.[3,4] At present, two salt-core manufacturing techniques are being developed: high-pressure squeezing with the use of the recrystallization process and shooting with the use of inorganic binders, e.g., alkaline silicates.[5,6] Considering the material-purchase costs for the production of salt cores from chemically pure salts, it is necessary to look for more suitable solutions for crating the basic salt matrix.

The aim of this paper is to verify the applicability of NaCl (from the vast range of the common salts commercially available in the Czech market), with the main focus on the possibility to replace the more expensive chemically pure salt with a cheaper common salt. The influences of various salt origins (rock, Alpine or sea salt), chemical compositions, shapes and surface morphologies of the grains on the mechanical properties (the bending strength) of the salt cores manufactured with the high-pressure squeezing and shooting methods are investigated.

2 SELECTION OF THE USED SALTS

To evaluate the cores manufactured with the squeezing and shooting methods, the tested cores were prepared from technical (common) and chemically pure (standard) salts. The salts for the core production were chosen according to the chemical composition declared by the manufacturer on the packaging (**Table 1**). From the wide range of commercially available salts six types of salts were finally chosen for the observation performed in this experiment. Each of the salts was of a different chemical composition, grain shape and surface morphology. These aspects and the selected salt-core-production technologies had significant influences on the final mechanical properties of the cores.

The chemical composition of the selected types of salts can be evaluated from two important viewpoints:

- Health
- Technology

With respect to health, salts contain healthy elements – iodine, fluorine – in the form of chemical compounds (KIO_3, KI, NaF) in the amount of 15–58 (max. 250) mg/kg. However, more important for the salt-core production is the technology (the chemical composition) that affects the quality of the manufactured cores. Some of the commercially available salts contain the additives that prevent the grains from sticking, i.e., the anti-sintering additives. These are K_2CO_3, $CaCO_3$, $MgCO_3$, SiO_2, $K_4[Fe(CN_6)] \cdot 3H_20$. Alpine salts feature substantial amounts of carbonates. These components added for the purposes of trouble-free storage, transport and manipulation have significant influences on the core-production technology and strength properties. The mechanisms of grain sticking and further recrystallization are disturbed and the strength of squeezed cores is decreased. Similarly, in the case of shot cores a decrease in the bending properties of the salt grains and alkaline silicate occurs.

3 MECHANICAL PROPERTIES OF SALT CORES

The criterion for evaluating the mechanical properties of squeezed and shot cores was the bending strength which was measured as follows:

- after 24 h in the air (the primary strength)
- after drying at 160 °C 1 h (105 °C 1 h)

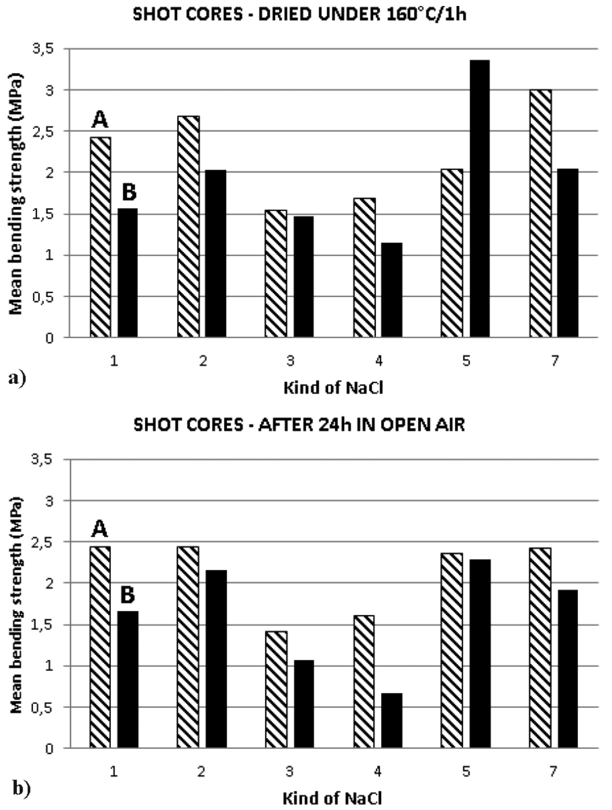

Figure 1: Comparison of the mean bending strengths of 6 types of shot salt: a) after drying and b) after 24 h in the open air (the mean value for 6 cores; A – original granularity, B – fraction of 0.063–1.0 mm)

Slika 1: Primerjava povprečne upogibne trdnosti 6 vrst vbrizganih soli: a) po sušenju in b) po zadržanju 24 h na zraku (srednja vrednost 6 jeder; A – originalna zrnatost, B – frakcija od 0,063 mm do 1,0 mm)

Table 1: Chemical compositions of the selected salts as declared by the manufacturers

Tabela 1: Kemijska sestava izbranih soli po navedbi proizvajalca

Salt sample	Commercial name	Additives		Presence of compounds
1	Rock salt with iodine and fluorine, edible (fine ground)	F I	max. 250 mg/kg 27 ± 7 mg/kg	NaF KIO_3
2	Rock salt with iodine (fine ground)	I	20–35 mg/kg	KI KIO_3
3	Alpine salt with iodine (vacuum packed)	NaCl $CaCO_3$ $MgCO_3$ KIO_3 I	98.8 % min. 0.9 % min. 0.2 % 33–58 mg/kg 20–34 mg/kg	$CaCO_3$ $MgCO_3$ KIO_3
4	Alpine salt with fluorine and iodine (vacuum packed)	NaCl $CaCO_3$ $MgCO_3$ KIO_3 I F	98.0 % min. 0.7 % min. 0.1 % 33–58 mg/kg 20–34 mg/kg max. 250 mg/kg	KIO_3 $CaCO_3$ $MgCO_3$ NaF
5	Fine sea salt with iodine (evaporated from sea water)	I	15–35 mg/kg	KIO_3
6	NaCl, p.a. (chemically pure)	Fe Heavy metals (Pb) SO_4 Ca Mg I Br	max. 0.0003 % max. 0.0005 % max. 0.005 % max. 0.005 % max. 0.002 % max. 0.008 % max. 0.01 %	

3.1 Shot cores

For the shot-core production a mixture of the originally supplied granulometry and a mesh fraction of 0.063–1.0 mm was used. The conditions for the shot-core production are as follows:

- Mixture composition: 100 mass parts of NaCl; 5 mass parts of Na – sodium silicate (M = 1.85)
- Hardening time: 50 s
- Core-box temperature: 190 °C
- Shooting speed: 7.5 s
- Air pressure: 7.5–8 bar

From **Figure 1** it is evident that for all the salts, except the sea salt with iodine (sample No. 5), the removal of dust proportion (< 0.063 mm) led to a bending-strength decrease. The final drying of the cores (160 °C/1 h) led to a bending-strength increase only for the NaCl sample (No. 5). Strengths comparable to the standard strength were achieved for rock salts with I and IF (Nos. 1, 2). The lowest strengths were achieved for the cores made of Alpine salt with I and IF (samples Nos. 3, 4). It was shown that the salt grain shape and the grain-surface quality are of the highest importance.

The apparent porosity *m* was calculated with the following relation:

$$m = \frac{\rho_{\mathrm{NaCl}} - \rho_{\mathrm{v}}}{\rho_{\mathrm{NaCl}}} \cdot 100\ (\%) \qquad (1)$$

where:
ρ_{v} = bulk density of cores (g/cm^3)

The apparent porosity of shot cores ranged from 35 % to 45 %. After sieving the dust (< 0.063 mm) off the apparent porosity, an increase (a decrease in the volume mass ρ_v and strength) occurred for all the salt samples except for sample No. 5 (sea salt with I), which underwent an extreme increase in the bending strength, especially after being dried at 160 °C 1 h **(Figure 2)**.

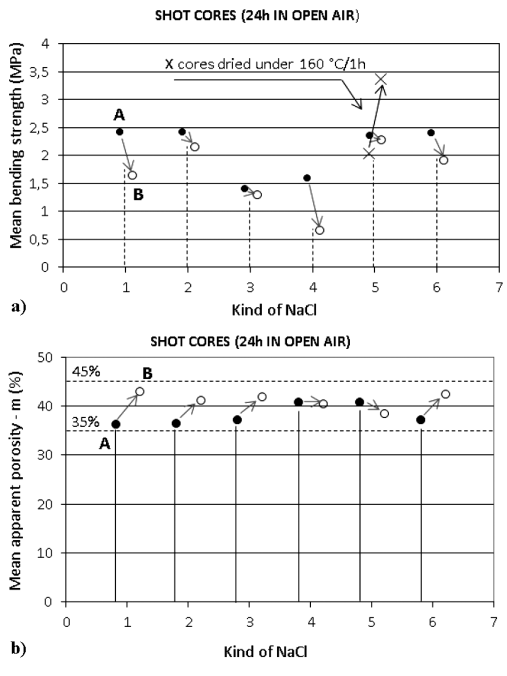

Figure 2: Comparison of: a) the mean bending strengths and b) apparent porosities of 6 types of shot salts after 24 h in the open air (the mean value for 6 cores; A – original granularity, B – fraction of 0.063–1.0 mm)

Slika 2: Primerjava: a) povprečne upogibne trdnosti in b) navidezne poroznosti 6 vrst vbrizganih soli po 24 h zadržanju na zraku (srednja vrednost 6 jeder; A – originalna zrnatost, B – frakcija od 0,063 mm do 1,0 mm)

3.2 Squeezed cores

For the production of squeezed cores, a mixture granulometry adjustment was carried out: the fraction of 0.063–1.0 mm. The conditions for the squeezed-core production are as follows:

- NaCl humidity: 0.65–1.04 %
- squeezing force: 200 kN
- squeezing tension: 104 MPa
- load rate: 9 kN/s

After the squeezing significantly higher strengths were achieved for all the salt samples **(Figure 3)**. The increase in the strength (together with a decrease in the apparent porosity) was evident for dried cores (105 °C 1 h). It was shown that the lowest strengths were achieved for the cores made of the salts with regular,

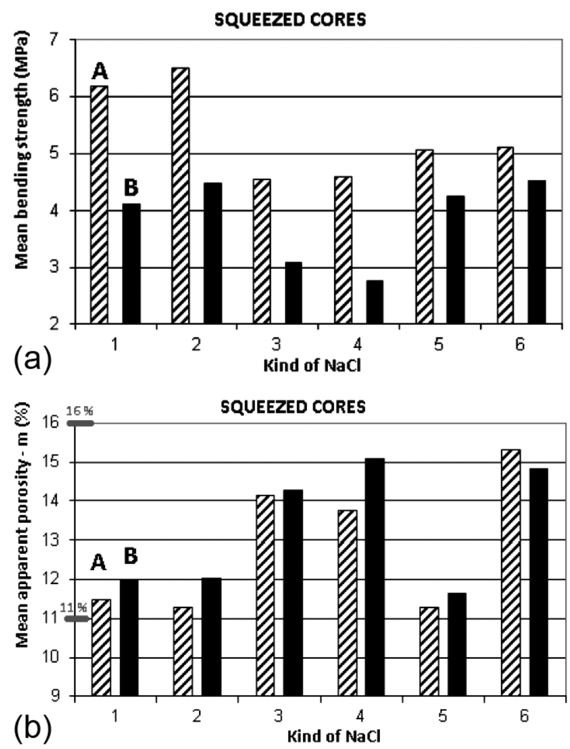

Figure 3: Comparison of: a) the mean bending strengths and b) apparent porosities of 6 types of squeezed salts (the mean value for 6 cores; A – cores additionally dried at 105 °C 1 h, B – 24 h in the open air)

Slika 3: Primerjava: a) povprečne upogibne trdnosti in b) navidezne poroznosti 6 vrst iztiskanih soli (povprečna vrednost 6 jeder; A – jedra dodatno sušena 1 h pri 105 °C, B – 24 h na zraku) cubic grain shape (Alpine salt, samples Nos. 3, 4 – recrystallized salts), whereas the highest strengths were achieved for the cores made of crushed-rock salts (samples Nos. 1, 2) and sea salt (sample No. 5). However, this does not apply to the standard salt (NaCl, p. a., sample No. 7). Regular, dipyramidal grain shape allows high strengths of the squeezed cores as well as of the shot ones. This shape is the closest to the globular silica-sand grain shape.

4 GRAIN SHAPE AND GRAIN-SURFACE MORPHOLOGY (SEM AND EDX ANALYSES)

A comparison of the chemical compositions declared on salt packagings and the real compositions determined with the use of an EDX microprobe is shown in **Table 2**.

In most cases, the grain shapes and surface morphologies of the selected salts vary significantly. The differences are due to different salt-production technologies, e.g., crushing and milling of the rock salt or the salt recrystallized from a solution – Alpine or sea salt. **Figures 4** to **7** below show grain shapes and surface morphologies, together with an EDX analysis of the investigated salts.

The differences between the salt-core strengths are explained with a detailed investigation of the salts using the SEM and EDX analyses. The low strengths of Alpine salts are caused by their lower quality of grain surfaces catching the blocking additives of $MgCO_3$ and $CaCO_3$; their presence was proven with the EDX analysis (**Figure 5**).

The dipyramidal grain shape of the chemically pure NaCl, p.a., is distinctive for its high grain coordination number, resembling the grain shape of SiO_2 sand grains, and being different from the regular, cubic Alpine-salt grains. This shape is more suitable for both core squeezing and core shooting.

Table 2: Comparison of declared chemical compositions and EDX microanalysis of the investigated real compositions
Tabela 2: Primerjava deklarirane kemijske sestave in EDX-mikroanaliza preiskovanih realnih sestav

	Type	Anti-sticking additives		F-additive	I-additive
COMPOSITION DECLARED BY THE MANUFACTURER	1 - Rock salt with iodine and fluorine (fine ground)			NaF	KIO_3
	2 - Rock salt with iodine, edible (fine ground)				KI, KIO_3
	3 - Alpine salt with iodine (vacuum packed)	$CaCO_3$	min. 0.9 %		KIO_3
		$MgCO_3$	min. 0.2 %		
	4 - Alpine salt with fluorine and iodine (vacuum packed)	$CaCO_3$	min. 0.7 %	NaF	KIO_3
		$MgCO_3$	min. 0.1 %		
	5 - Fine sea salt with iodine (evaporation of sea water)				KIO_3
	7 - NaCl, p.a. (chemically pure)				
		Elements observed with the EDX microprobe			
EDX ANALYSIS	1 - Rock salt with iodine and fluorine (fine ground)	Mg, C, O		F	
	2 - Rock salt with iodine, edible (fine ground)	Ca, C, O			K
	3 - Alpine salt with iodine (vacuum packed)	Mg, Ca, C, O			K
	4 - Alpine salt with fluorine and iodine (vacuum packed)	Mg, Ca, C, O		F	K
	5 - Fine sea salt with iodine (evaporation of sea water)	Mg, Ca, Si			K
	7 - NaCl, p.a. (chemically pure)				K

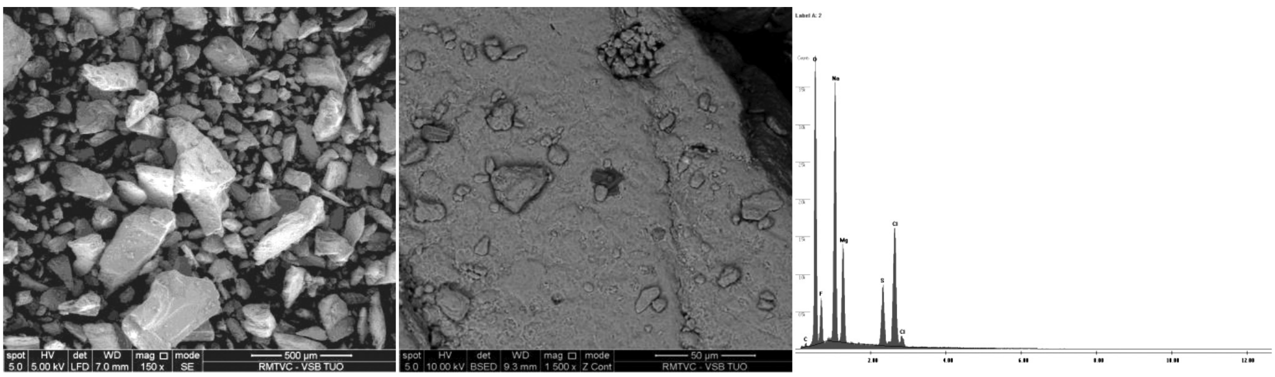

Figure 4: Shattered surface of crushed-rock salts (samples Nos. 1, 2) and EDX analysis of its chemical composition
Slika 4: Razbita površina drobljene kamene soli (vzorca št. 1 in 2) in EDX-analiza kemijske sestave

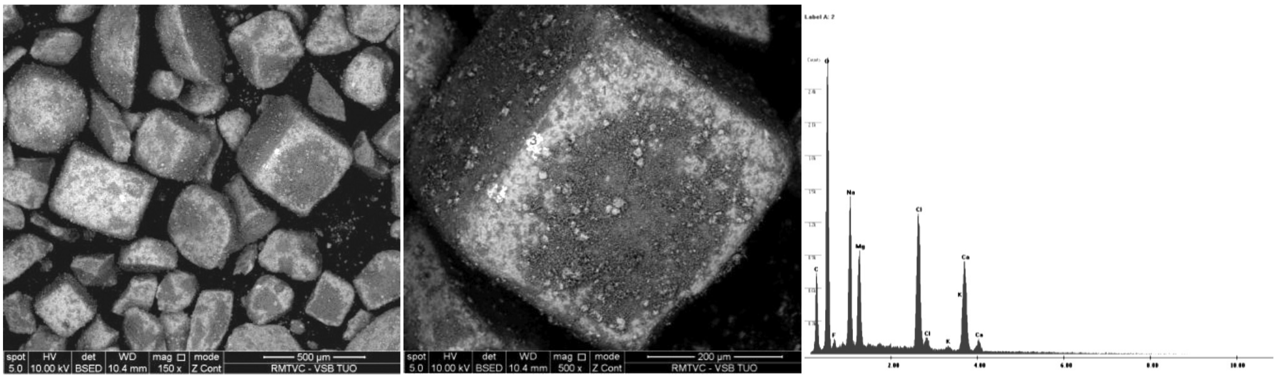

Figure 5: Regular cubic grains of Alpine salts (samples Nos. 3, 4) and EDX analysis confirming the presence of anticaking agents on the salt grain surface ($MgCO_3$, $CaCO_3$)
Slika 5: Pravilna kockasta zrna soli Alpine (vzorca št. 3 in 4) in EDX-analiza, ki potrjuje prisotnost sredstva proti sprijemanju na površini zrn soli ($MgCO_3$, $CaCO_3$)

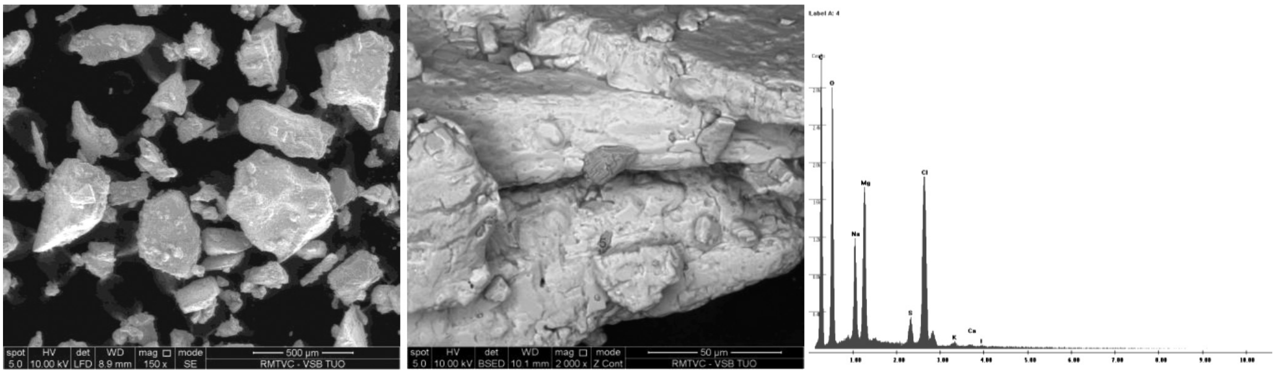

Figure 6: Oval form of sea-salt grains (sample No. 5) and EDX analysis of its chemical composition
Slika 6: Ovalna oblika zrn morske soli (vzorec št. 5) in EDX-analiza kemijske sestave

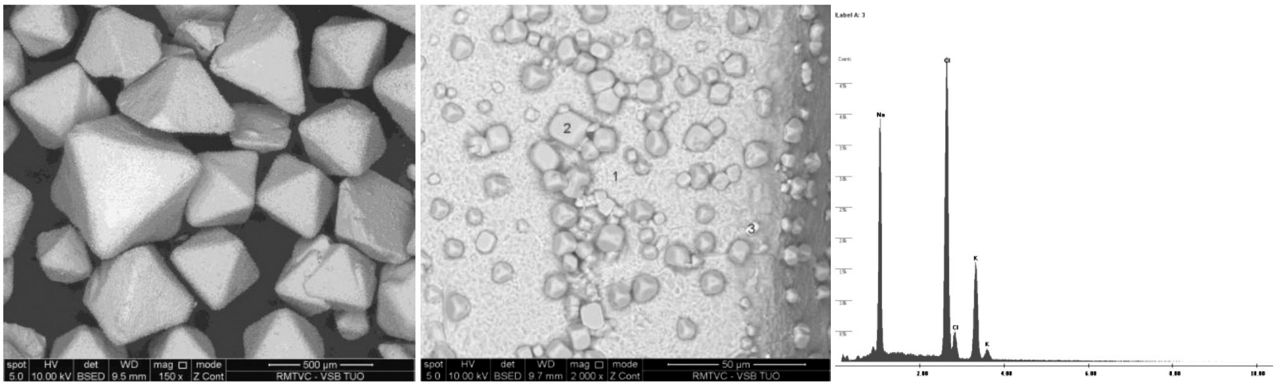

Figure 7: Regular dipyramidal form of NaCl, p. a. – standard (sample No. 7) and EDX analysis of its chemical composition
Slika 7: Dvopiramidna pravilna oblika NaCl, p. a. – standard (vzorec št. 7) in EDX-analiza kemijske sestave

5 HYGROSCOPICITY OF CORES

Hygroscopicity of common-salt cores and chemically pure salt cores was investigated using the weight-change measurement. The cores were stored in various climate conditions including the humidity of 35–58 % RV, the temperature of 20.7–24.9 °C and normal pressure. Hygroscopicity was observed for 23 d.

The results of the measurements given in **Figure 8** show different hygroscopic behaviours of squeezed and shot cores. The porosity and, at the same time, the strength of the cores are considerably influenced by the used manufacturing technology. It is evident that the hygroscopicity increases with the growing porosity (shot cores) while the strength is on a decrease. In the case of a lower porosity, hygroscopicity is less evident for the squeezed cores. But in both cases the growth of weight is not considerable, only sufficient for short-time storing

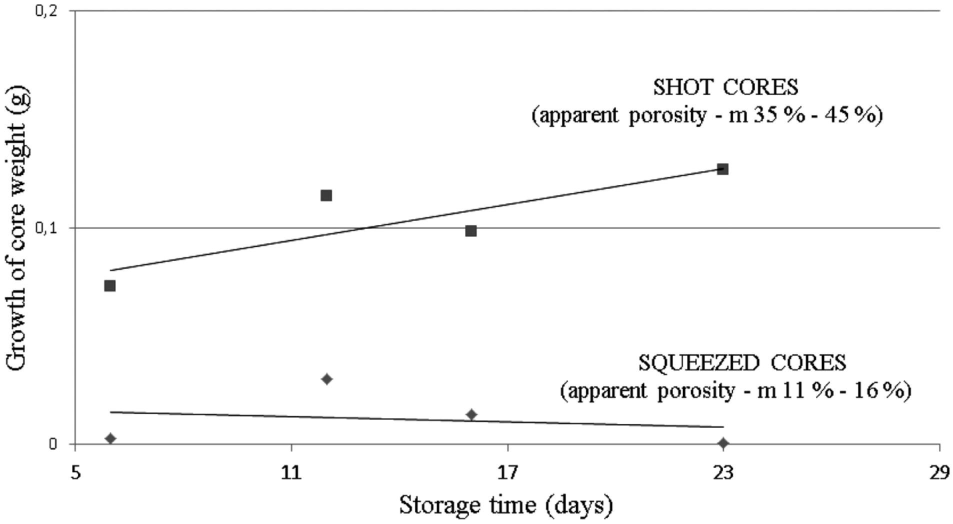

Figure 8: Different hygroscopicity trends for squeezed and shot cores
Slika 8: Različna usmeritev higroskopičnosti iztisnjenega in vbrizganega jedra

the salt cores destined for immediate use in the manufacturing process of castings.

6 INFLUENCE OF PRODUCTION TECHNOLOGY ON THE SALT-CORE POROSITY

The actual porosity, the pore size and pore distribution, was measured with a Micromeritics Instrument Corporation mercury porosimeter investigating the salt cores, based on NaCl and squeezed with a pressure of 200 kN (104 MPa) or shot with a pressure of 7.5–8 bar. The results are shown in **Table 3**.

Table 3: Properties of different salt cores
Tabela 3: Lastnosti različnih jeder iz soli

	Sample	Total volume of pores (cm^3/g)	Mean diameter of pores (μm)	Porosity (%)	Bulk density (g/cm^3)
Shot	2	0.1482	0.3240	24.20	1.6329
	5	0.1443	0.4207	23.52	1.6299
	7	0.2278	0.2409	19.10	0.8383
Squeezed	2	0.0320	0.2416	6.51	2.0351
	5	0.0354	0.2216	6.98	1.9734
	7	0.0635	0.5525	12.06	1.8977

The porosity of the squeezed cores is 6–12 % (a correlation with the apparent-porosity calculated value) while the porosity of the shot cores is 19–24 %, i.e., about four times higher. The overall volume of pores is one order lower for the squeezed cores.

From the resulting values it is evident that the applied production technology has a significant influence on the core actual porosity. This is important for the penetration of metal into the cores, especially in the case of high-pressure die casting, where the cores are extremely stressed by the metal pressure.

7 DISCUSSION

On the basis of the results achieved during the investigation of commercial salts (different origins, granulometries, grain shapes and chemical compositions) the following can be stated:

- In all the cases the cores made with the squeezing method achieved 2–3 times higher bending strengths than the shot cores (**Figure 4**). They had a lower hygroscopicity (lower porosity) and lower water solubility so that only simple geometrical forms can be manufactured with this method.
- Shot cores are highly water soluble. It is possible to utilize the existing shooting-core foundry machines. However, there is a negative aspect of the high hygroscopicity correlating with the porosity and it is, therefore, necessary to protect the core surfaces against the penetration with coatings and lubricants.
- Due to the removal of the parts < 0.063 mm in the case of all the cores, the apparent porosity increased and the strength decreased, with the exception of sample No. 5 – the sea salt. An explanation is offered involving the granulometry of the bought sea salt that contained, unlike the other salts, almost no dust parts. The grains are highly oval, having no sharp edges.
- Dipyramid (sample No. 7 – standard) seems to be the most suitable grain shape giving high strengths to both the shot cores and squeezed ones. It enables the highest coordination number of the grains and, most of all, it is close to the shape of the SiO_2 base sand. For that reason this shape seems to be advantageous for squeezing and shooting the cores.
- An adverse influence of the anticaking agents ($CaCO_3$, $MgCO_3$, SiO_2, $K_4[Fe(CN_6)]·3H_2O$) in combination with the regular, cubic shape of Alpine salts resulted in a strength decrease for both methods of the core production (squeezing and shooting). The

presence of undesirable additives on the grain surfaces does not enable binding with alkali silicate (shooting) and sticking of the grains with the following recrystallization along the grain boundaries (squeezing).

8 CONCLUSION

The aim of the research was to investigate the possibility of replacing the expensive chemically pure salt with common salt for the production of foundry cores applied in gravity, low-pressure, and possibly also high-pressure die casting of non-ferrous alloys.

The best strength results were achieved for crushed salts (rock salt) used for squeezing and shooting. The occurrence of fine-dust fractions contributes to achieving higher core strengths. The salts with recrystallized grains (Alpine salts) of a regular, cubic shape are less suitable, with the exception of dipyramidal shapes (chemically pure salts). Additions of the anti-sintering additives (SiO_2, $MgCO_3$, $CaCO_3$, $K_4[Fe(CN_6)]\cdot 3H_2O$) (for Alpine salts) deteriorate the strength properties.

A comparison of the core-production methods shows that the squeezed cores have higher mechanical properties (the bending strength) and the minimum hygroscopicity (decreased actual porosity).

The investigation proved that chemically pure salt can be adequately replaced with rock salt that is up to 50-times cheaper.

Acknowledgement

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