

T. SEBŮK*, M. VONDRUSKA*, V. BEDNARIK*, K. KULISEK**

LEACHING OF POLLUTANTS FROM SOLIDIFIED FLYING ASH WITH HIGH CONTENT OF CALCIUM SULPHATE AND CALCIUM OXIDE

The influence of composition of solid specimens prepared from fluidised bed combustion product, two types of cement binders and NaCl (as a chosen pollutant) on the conductivity and on Na⁺ and Ca²⁺ ions' content in leachate were studied for 360 days. NaCl causes a considerable increase of compressive strength and its content is decisive for conductivity of leachate up to 360 days of leaching. About 50% of the sodium ions from NaCl are gradually leached from solid sample after one year of leaching.

1. INTRODUCTION

The solidification of grainy waste products is used in practice. The solid structure of a common flying ash may be formed using a low dose of cement or lime as alkali activators. The way of creating the solid matrix of activated flying ash depends on its chemical composition. Fluidised bed combustion products obtained by combustion of powdery mixture of coal and limestone contain various amounts of CaO and CaSO₄. Both compounds react with water present on landfills. Such a process occurs during solidification as well as in the solidified waste. Our results not included here showed that CaO is rapidly transformed to Ca(OH)₂ and CaSO₄ is transformed to CaSO₄·2H₂O within several days of interaction with water. Moreover, high content of gypsum supports the creation of ettringite – 3CaO·Al₂O₃·CaSO₄·13H₂O. All those products of hydration have markedly greater volume than the compounds before reaction and may contribute to disintegration of the solid structure. Consequently, leaching of toxicants from disintegrated wastes may increase markedly owing to the increase of total specific surface area of solid particles. The creation of ettringite is mainly connected with the danger of destruction. According to the kinetics of solid structure creation [1]–[3]

*VUT, Faculty of Technology, Masarykovo náměstí 275, 762 72 Zlín, Czech Republic, email: sebok@volny.cz.

** VUT, Faculty of Civil Engineering, Veveri 95, 662 37 Brno, Czech Republic.

the solidification may be very favourably influenced by addition of NaCl into the samples of flying ash (figure 1). The creation of ettringite is depressed and the morphology of crystals is influenced by the presence of chloride ions. Considerable amount of inorganic salts is produced in incinerators where solution of NaOH is used for sprinkling of waste gases. They can be discharged in liquid or powdered form. Very pure NaCl is for instance discharged from incinerators fitted for combustion of polyvinyl chloride or other chloride-type waste products. Use of the salt as a secondary raw material and also the possibility of its storing in landfills are very limited. Therefore the potential possibility of the salt disposal together with solidified flying ashes seems to be very interesting [4], [5]. Moreover, the creation of ettringite may be favourably influenced by this precaution. The main problem of NaCl application as an additive is the leaching of its ions to environment. Therefore the influence of the composition of solidified waste, properties of binder and time on the leaching of this pollutant from solid samples was studied.

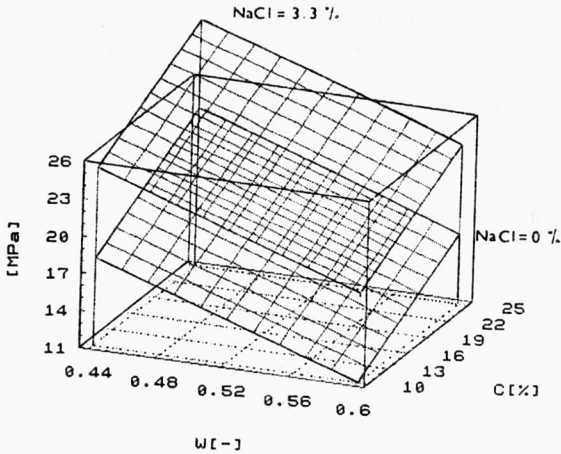


Fig. 1. Compressive strength of solidified samples after 28 days versus water to solid compounds ratio (W) and dose of the cement S (C); minimal and maximal doses of NaCl expressed in % of the mass of solid compounds

It is a well known fact that the conductivity change of the leachate depends on the kinetics of ion diffusion from the solid sample. It also depends on the rate of moistening the surface of capillaries and pores of a solid body. Volume of water penetrating into solid porous structure of immersed sample depends on the porosity of sample and on the parameters of capillary network in the structure. Penetrating water compresses the air in capillaries and therefore the process of wetting is long. The main variable influencing the kinetics of water penetrating into capillaries depends on variables in the following Poiseuille's equation

$$Q = \frac{\pi r^4 p l \tau}{8 \eta L},$$

where: Q – volume of penetrating water (m^3/s), r – radius of capillary (m), pt – pressure of air in the capillary (Pa), L – length of capillary (m), η – viscosity of liquid (Pa·s), τ – time (s).

The capillary network in solid body is complicated and therefore the above equation can be used only for the illustration of processes studied. It seems that the total porosity of the sample is essential. But more important are the characteristics of capillaries creating the flow network for the movement of water and the transport of ions in the direction of concentration gradient.

2. EXPERIMENTAL PART

2.1. THE AIMS OF THE TESTS

One of the aims of the test was to find the relationships between the composition of solidified samples containing: flying ash + different cement binder + NaCl dose, and some chosen parameters of leachate in early and late phases of leaching. The next aim was to determine the diffusion rate of sodium and calcium ions from solid specimens to leachate under the standard conditions of the tests and to determine the proportions of Na^+ ions bond in structure of hydration products to Na^+ ions present in the leachate.

2.2. FLYING ASH

Fluid flying ash (fluidised bed combustion product = FBC-P) from a central heating plant in Zlin (Czechia) was used for the tests. Basic parameters and the results of X-ray analysis (apparatus Philips APD 15) are listed in tables 1 and 2. The content of main compounds was estimated (% b.w.) as follows: quartz – 6%, CaSO_4 – 18%, hematite – 3.5%, CaO – 8.1%. The content of periclas, calcite, feldspar and portlandite was estimated up to 5%.

Table 1

Basic parameters of fluidised bed combustion product

Volume weight (g/cm^3)	Density (g/cm^3)	(mS/m)	pH	Chlorides (mg/dm^3)	Sulphates (mg/dm^3)	PAH* (ng/dm^3)	F^- (mg/dm^3)	PO_4^{3-} (mg/dm^3)
Solid		Leachate, solid:liquid = 1:10 after 24 hours of standard leaching						
0.902	2.176	1193	12.65	150	1675	< 26.2	3	10

*PAH – polyaromatic hydrocarbons (12 pollutants).

Table 2

Results of X-ray diffraction analysis of ash – height of the peaks of diffractions
in number of division lines of the recording paper

Quartz	Hematite	CaSO ₄ II	CaO	Calcite	Feldspar	Ca(OH) ₂	Clay	Periclas
20.9	20.1	70.8	67.0	17.8	15.6	10.8	10.1	18.2

2.3. CEMENT

Two binders were prepared by grounding the clinkers from two different cement works in a laboratory ball mill. The contents of main minerals are shown in table 3. The clinkers used were chosen deliberately for a markedly different C₃A content. Specific surface area of both binders was about 450 m²/kg after Blaine. The binders were gypsum-free because of a sufficient content of calcium sulphate in the ash. One of the aims of the tests was to remove calcium sulphate occurring in high concentration in the ash by its chemical reaction with compounds of binders.

Table 3

Composition of clinkers by optical method

Compound	Cement S	Cement M
C ₃ S	67.00	77.21
C ₂ S	14.20	6.4
C ₃ A	10.1	1.15
C ₄ AF	8.6	15.02
CaO free	0.1	0.21
Total (%)	100.0	99.99

2.4. NATRIUM CHLORIDE

NaCl was used as a model toxicant because of its good solubility. Na⁺ ions have also small diameters and therefore easily diffuse from solid body to liquid phase during leaching tests. It is also well known that NaCl has an accelerating effect on cement hardening. Two samples were tested. The first one was NaCl p.a. The second one was the powdered salt from a waste incinerator (see table 4). Very similar results concerning the influence of the salt dose on the compressive strength for both types of salts were obtained. Besides, both the results of leaching tests and the relationships obtained were very similar. The results presented in this article were obtained using NaCl p.a. for a better reproducibility of the parameters of the samples tested.

Table 4

Basic parameters of salt from incinerator

Parameter	Unit	Value
Weight loss 105 °C	(%)	0.64
Ignition loss 950 °C	(%)	0.81
NaCl content	(%)	89.1
Other soluble compounds (11)	(%)	0.9
Insoluble compounds	(%)	10.1

2.5. PREPARATION OF SAMPLES

Mixtures were prepared from FBC-P, cement, water and NaCl using a laboratory mixer. Cubes of 25 mm edge were prepared. After 24 hours of hardening the cubes were demoulded and stored for 28 days at humidity ranging from 80 to 90% and a temperature from 21 to 23 °C. After 28 days the samples, whose compressive strength had to be determined, were stored in water as long as necessary. The composition of samples is shown in table 5.

Table 5

Composition of specimens. Solid compounds (binder and ash)

Specimen No.	Ratio of water : solid compounds W	Cement content (%) in the mass of solid compounds	NaCl content (%) in the mass of solid compounds
1	0.48	14	0.45
2	0.60	14	0.45
3	0.48	26	0.83
4	0.60	26	0.83
5	0.48	14	1.78
6	0.60	14	1.78
7	0.48	26	3.30
8	0.60	26	3.30
9	0.44	20	1.60
10	0.64	20	1.60
11	0.54	10	0.80
12	0.59	30	2.40
13	0.54	20	0.00
14	0.54	20	3.20
15	0.54	20	1.60

2.6. LEACHING TESTS

One cube was selected from each series presented in table 5. After 28 days of storing under conditions specified above the cube was immersed in redistilled water. Solid to liquid ratio was 1:10 b.w. The conditions of the tests were similar to those that might be in the landfill with solid bodies of the ash saturated with ground water. Therefore the content of a vessel was not agitated. The conductivity of leachate and the content of Na^+ and Ca^{2+} ions were determined in chosen terms.

2.7. FLAME ATOMIC ABSORPTION SPECTROSCOPY

Apparatus spectrophotometer GBC933AA (GBC Scientific Equipment Pty Ltd.) was used to determine the content of Na^+ and Ca^{2+} ions in the solution after leaching.

2.8. REGRESSION ANALYSIS

Computer program Statgraphics 2 (product of Statistical Graphic Corporation USA) was used to determine how the dependent variables tested depended upon the independent variables. Every correlation was assessed based on the limits of the coefficient of multiple determination R^2 . $R^2 < 30\%$ – no or low correlation, R^2 ranging from 30% to 60% – rather high correlation and $R^2 > 60\%$ – very high correlation between the variables tested.

3. EVALUATION OF RESULTS

The results chosen (figure 1) indicate that compressive strength of solidified samples of FBC-P decreases with the increase in the water to solid compounds ratio and the increase in the doses of cement and NaCl. Similar relationships were obtained after 1 and 2 years of a sample hardening in water.

Figure 2 shows that shortly after interaction of distilled water with the surfaces of sample, pores and capillaries, the diffusion of ions starts in direction of concentration gradient. Conductivity of leachate from solidified ash without cement and NaCl reaches its maximum within several ten hours as is shown in figure 3. Further changes are not significant up to 360 days of leaching. Conductivity of leachate from the samples with cements S and M (their composition is shown in table 5, No. 8) is markedly higher in comparison with that from solidified ash in all terms. The cements used cause only slight differences in conductivity. In this case, the conductivity reaches its maximal value after several days as well. Further changes are also insignificant up to term of 360 days. Conductivity of the leachate from other samples (table 5) varies – there is a substantial difference between its lower limit represented by the conductivity of solidified ash without cement and NaCl and its upper limit represented by the conductivity of samples with two types of cement and maximal dose of NaCl (figures 2, 3).

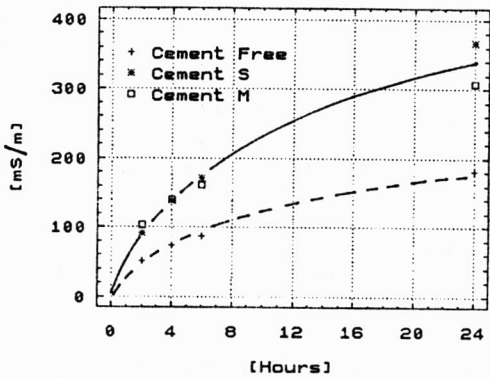


Fig. 2. Conductivity of leachate obtained by leaching of solidified ash without binder and ash with cements S and M in the dose of 250 g per 1 kg of ash versus time of leaching

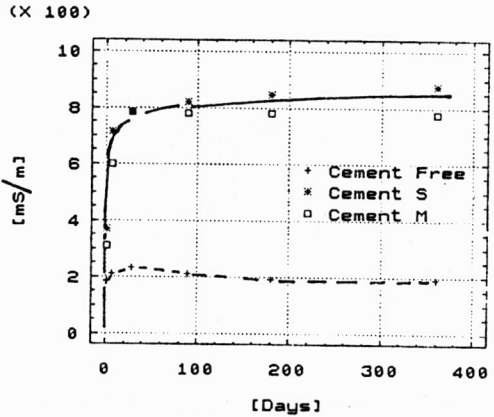


Fig. 3. Conductivity of leachate (solid : liquid = 1:10) obtained by leaching of solidified ash without binder and ash with cements S and M in the dose of 250 g per 1 kg of ash versus time of leaching

Composition of solidified samples influences the conductivity of the leachate as it is evident from figures 4–7. Rather high and very high correlations between the variables tested are presented in figures 4 ($R^2 = 49.5\%$), 5 ($R^2 = 96.37\%$), 6 ($R^2 = 63\%$), 7 ($R^2 = 93.4\%$). They can be derived from the correlation coefficients obtained. The increase of mixing water causes a small increase in the conductivity. The consistencies of suspensions for the preparation of samples were chosen in the range from plastic to fluid. The increase of a dose of the cements tested causes a considerable increase of the leachate conductivity. The leachate from the samples with cement S has higher conductivity within 24 hours than that with cement M (figures 4 and 6). This is probably caused by leaching of cement compounds in early stage of hydration. The differences are minimal after 360 days of leaching (figures 5 and 7).

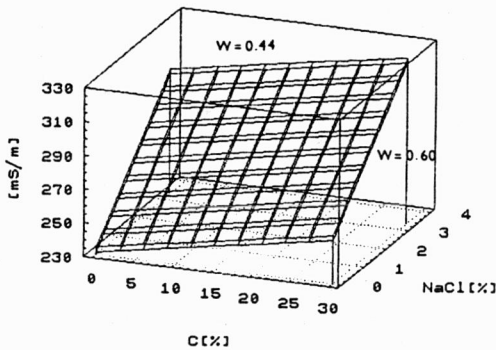


Fig. 4. Conductivity of leachate after 24 hours versus doses of cement S and NaCl, both in % of the mass of solid compounds.
W – water : solid compounds ratio by weight

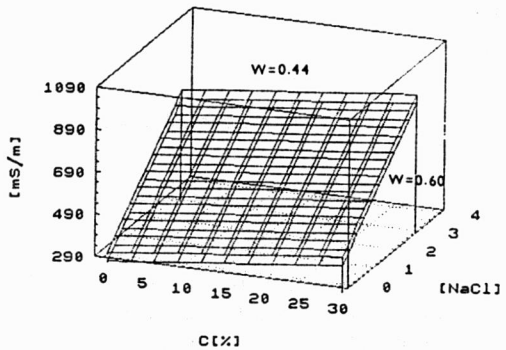


Fig. 5. Conductivity of leachate after one year of leaching versus doses of cement S and NaCl, both in % of the mass of solid compounds.
W – water : solid compounds ratio by weight

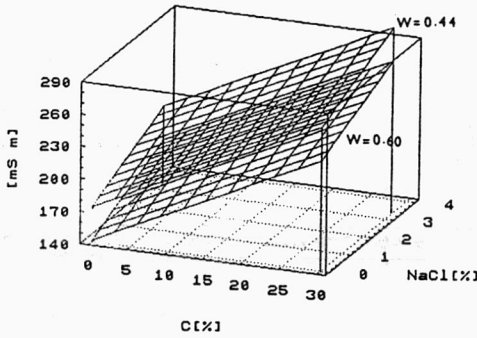


Fig. 6. Conductivity of leachate after 24 hours of leaching versus doses of cement M and NaCl, both in % of the mass of solid compounds. W – water : solid compounds ratio by weight

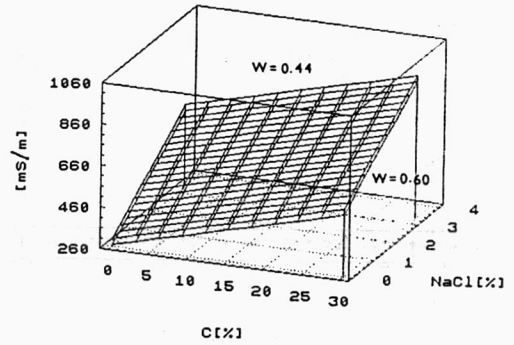


Fig. 7. Conductivity of leachate after one year of leaching versus doses of cement M and NaCl, both in % of the mass of solid compounds. W – water : solid compounds ratio by weight

The content of Na^+ and Ca^{2+} cations in the leachate contributes to the increase of its conductivity (figures 8–11) by portion 62.5%, 94.2%, 67.4%, 97.8%. Remaining portions up to 100% represent the contribution of other dissociated compounds. Calcium ions contribute markedly to the conductivity of the leachate after 24 hours of leaching (figures 8, 10) owing to their high content in it. The concentration of calcium ions decreases markedly in the leachate after one year of leaching and therefore their influence on the conductivity is very slight and the conductivity increases linearly with the content of sodium ions (figures 9, 11).

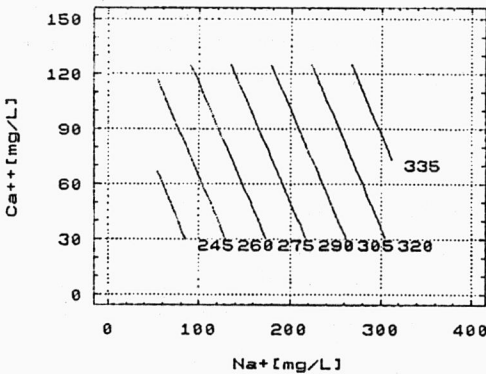


Fig. 8. Conductivity of leachate after 24 hours of leaching of samples with cement S versus Na^+ and Ca^{2+} content

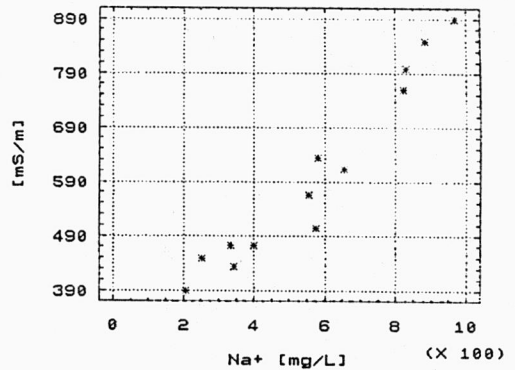


Fig. 9. Conductivity of leachate after one year of leaching of samples with cement S versus Na^+ content

Results in figure 12 show that about 80% of Na^+ ions from NaCl are bound in a structure of sample after 24 hours of leaching. This per cent decreases to about 50%

after 360 days of leaching (figure 13). The absolute amount of Na^+ ions in the leachate increases linearly with the increase of an initial dose of NaCl in the sample.

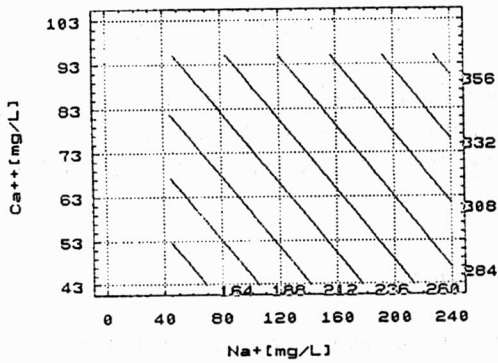


Fig. 10. Conductivity of leachate after 24 hours of leaching of samples with cement M versus Na^+ and Ca^{++} content

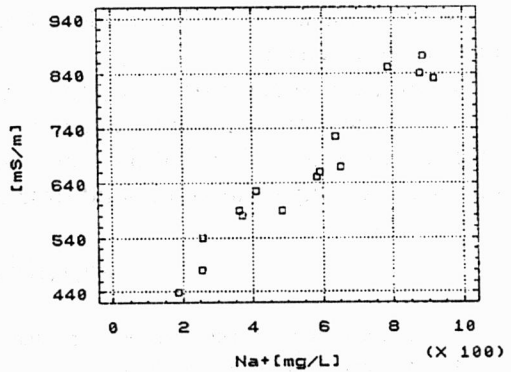


Fig. 11. Conductivity of leachate after one year of leaching of samples with cement M versus Na^+ content

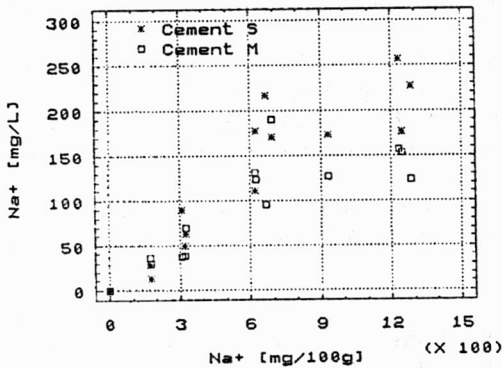


Fig. 12. Content of Na^+ ions in the leachate after 24 hours of leaching versus initial content of the same ions in the solid sample with cements M and S

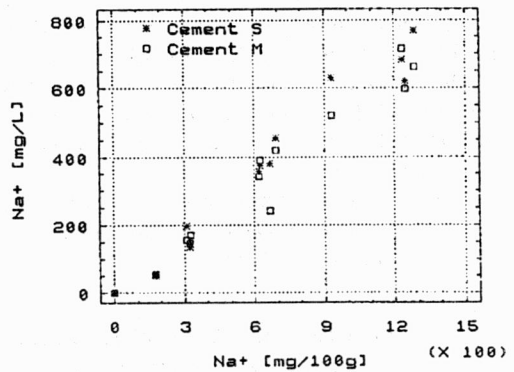


Fig. 13. Content of Na^+ ions in the leachate after one year of leaching versus initial content of the same ions in the solid sample with cements M and S

A kind of the cement used has only a small effect on the process studied. It seems that the process of Na^+ diffusion is gradual. All Na^+ ions are not irreversibly bound in a crystallic structure of hydrates. Based on the results obtained it is not possible to determine the proportions between reversible and irreversible bonds of Na^+ ions.

4. CONCLUSIONS

- The composition of the solidified samples influences their parameters. The decrease of mixing water content causes an increase of compressive strength and a decrease of conductivity of leachate mainly in the first phase of leaching.

- The increase of cement content is associated with the increase in both concentration of leached components and leachate conductivity. Mineralogical composition of cements has only a slight influence on the conductivity determined.

- The presence of NaCl considerably increases the compressive strength and conductivity of leachate.

- Diffusion of Na⁺ from solid structure of samples gradually grows in all terms of the tests. Linear relationship between the content of Na⁺ ions in the sample and in the leachate was found after 360 days of leaching. It seems that only small part of Na⁺ ions is irreversibly bond in the solid structure.

ACKNOWLEDGEMENT

This research was partially supported by the Czech Grant Agency, grants No. 104/99/1565 and 103/00/1185. Authors thank for the support.

REFERENCES

- [1] KAMON M., KATSUMI T., *Utilization of coal fly ash from fluidized bed combustion systems*, Geoenvironment, 1995, 2000, ASCE, pp. 1765–1779.
- [2] BEHR-ANDERS C.B., HUTZLER N.J., *Characterization and use of fluidized bed combustion coal ash*, Journal of Environmental Engineering, 1994, Vol. 120, No. 6, pp. 1488–1506.
- [3] BLAND A. E., *Pressurized fluidized bed combustion ash*. Part I. *Fuel*, 1997, Vol. 76, No. 8, pp. 733–740.
- [4] SEBŐK T., *Influence of NaCl on the strength of samples with flying ashes*, Research report, Stavební výzkum, 1997.
- [5] KNOLL K.L., BEHR-ANDERS C.B., *Fluidized bed combustion ash for the solidification and stabilization of a metal hydroxide sludge*, Journal of the Air & Waste Management Association, 1998, Vol. 48, No. 1, pp. 35–43.

ŁUGOWANIE ZANIECZYSZCZEŃ Z ZESTALONEGO POPIOŁU LOTNEGO O DUŻEJ ZAWARTOŚCI SIARCZANU WAPNIA I TLENKU WAPNIA

Przez 360 dni badano wpływ składu stałych próbek przygotowanych z produktu spalania złoża fluidalnego, dwóch rodzajów spoiw cementu i chlorku sodu (wybrane zanieczyszczenie) na przewodnictwo właściwe odcieku po ługowaniu i na zawartość w nim jonów sodu i wapnia. Obecność chlorku sodu powoduje wyraźne zwiększenie wytrzymałości próbek na ściskanie i decyduje o przewodnictwie właściwym odcieku po ługowaniu aż do 360. dnia ługowania. Po upływie roku około 50% jonów Na⁺ z NaCl zostaje stopniowo wylugowanych ze stałej próbki.