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ABSTRACT

The influence of organic solvents in nitrate waste streams is investigated concerning the physical, chemical and mechanical properties of the full size waste forms when ordinary Portland cement is used as a binder matrix. Simulated waste streams containing sodium nitrate varying from 0 to about 26 wt %, including tributyl phosphate/dodecane, 30/70, as the organic phase varying from 0 to 10 wt %, were assayed.

IMOBILIZAÇÃO DE FLUXOS DE REJEITOS CONTENDO NITRATOS E PEQUENAS QUANTIDADES DE SOLVENTES ORGÂNICOS

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RESUMO

É investigada a influência da presença de solventes orgânicos, em fluxos de rejeitos contendo nitratos, nas propriedades físicas, químicas e mecânicas da forma final do rejeito imobilizado quando cimento Portland é usado como matriz de imobilização. Foram simulados fluxos de rejeito contendo nitrato de sódio variando de 0 a 26 %, em peso, e incluindo tributil - fosfato/dodecano, 30/70, como fase orgânica em quantidades variando de 0 a 10 % em peso.

INTRODUCTION

Hydraulic cements are quite convenient binder materials to immobilise inorganic low- or intermediate-level waste streams. The nuclear area which comprises nuclear centers, research establishments and others generates, besides radioactive aqueous waste streams, also organic wastes, with volumes relatively smaller. Higher volumes are produced in the nuclear fuel cycle as consequence of the reprocessing of spent fuel elements.

Usually the organic chemicals wastes are lubricating fluids, solvents or diluents occurring in extraction experiments, scintillation cocktails from analytical laboratories and miscellaneous solvents from decontamination processes.

Those organic chemicals coming from research laboratories contain low levels of beta/gamma activity and those arising from the reprocessing of spent fuel are contaminated also with alpha emitters or fission products and actinides.

A question arises, however, if small amounts of different types of organics which can accompany the inorganic phase deteriorate the properties of the end product. That impurity happens to occur when large tanks are used to store the wastes. The thin film of organics which rests on the surface of the inorganic phase becomes laborious to be removed.

Very little informations exist about the effects of organics chemicals on the cement matrix. This occurs in part due to the vast number of possible chemicals present in the waste streams.

The treatment of such mixed wastes is somewhat problematic because some changes in the early stage of the final waste form properties, production of new chemical species due to the radiation, early and late deleterious chemical interactions between all constituents, including cement compounds and degradation of organics by micro-organisms may succeed.

The organic chemicals present in waste streams are more complex if compared with those ones traditionally used in civil engineer constructions whose main fate does not disturb late age properties. The involved chemistry between waste solvents and cement is not the aim of this work but clearly it can not be done an oversimplified picture for this kind of wastes since time scaling of the final product must be taken into account.

This work aims to obtain general informations on the conditioning of mixed phase wastes for interim storage as well as for final disposal. For this purpose the chosen organic phase was a mixture of tributyl phosphate and dodecane in 30:70 wt % proportion. Physical, chemical and mechanical properties were studied in laboratory scale experiments.

EXPERIMENTAL PROCEDURES AND RESULTS

Laboratory scale samples were prepared using ordinary Portland cement with chemical composition given in Table I. Mixtures with water to cement ratio, W/C, equal to 0.30; 0.40 and 0.50 were assayed. Sodium nitrate was used to simulate the main component of the inorganic waste stream, with weight percentage varying from 0 to 26 %. The organics, TBP/DOD, were added to the simulated waste stream in the proportion of 0, 2, 5 and 10 % by weight.

All the mixtures were prepared using a planetary paddle mixer and poured inside specific molds for each kind of test. The specimens were unmolded after 24 h and stored, at room temperature, during 28 days in airtight containers before testing, according the specific standards. Each result represents the average of four samples.

Table I - Ordinary Portland cement composition

Compound	Total amount (%)
CaO	63.20
SiO_2	20.50
Al_2O_3	5.46
Fe_2O_3	3.24
MgO	2.32
SO_3	1.86
Na_2O	0.06
K_2O	0.68
TiO_2	0.20
CaO - free	0.60
Alkali content	0.51
Ignition loss	2.48
Insolubles	0.80

The homogeneity of the prepared samples was confirmed by use of a technique described elsewhere (1). For that purpose TBP/DOD contaminated with uranium was used to investigate at same time the distribution of the organic phase into the cement matrix as well the homogeneity of the mixture.

A typical result of the normal cumulative distribution for a tracer placed into the cement paste is shown in Figure 1.

The cement setting time varies according to several parameters such as cement age, storing conditions, chemical composition, chemicals amount in the final formulation which

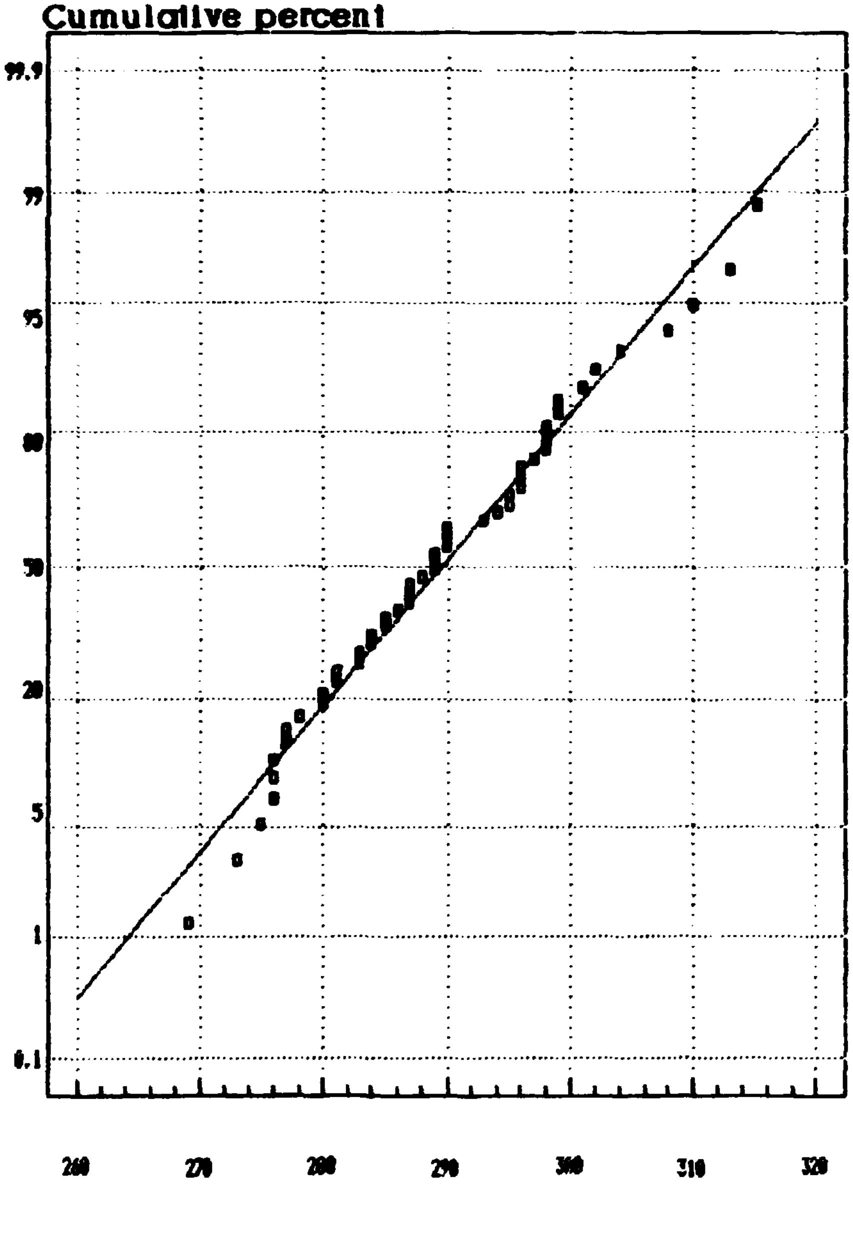

Figure 1 - Normal probability plot for W/C = 0.35, $NaNO_3$ = 14 wt % and TBP/DOD = 6 wt %

can accelerate or retard the setting etc. In the present work different percentages of organics and nitrates were assayed resulting in initial settings varying from 198 to 450 min while the final setting time varied from 270 to 625 min.

Setting was measured using a manual Vicat apparatus. Initial and final setting times were determined in fresh pastes under controlled room conditions. The obtained results are shown in Figures 2, 3 and 4.

All formulations were assayed for free standing water 24 h after the mixing procedure.

Integrity tests were made with specimens of cylindrical shape with 71 mm diameter and 71 mm height after 28 days of sealed cure. Those tests permitted to verify that the organic phase does not segregate from the cement matrix by water immersion. Only for the higher organic content as well W/C ratio was possible to detect slight greased phase in few points onto the specimen surface. Those receipts were neglected for setting time and porosity measurements.

An open flame test was applied to all specimens with organic load. The open flame from butane torch was contacted with the samples for some few seconds. The extinction occurred as soon as the flame was removed and none of the

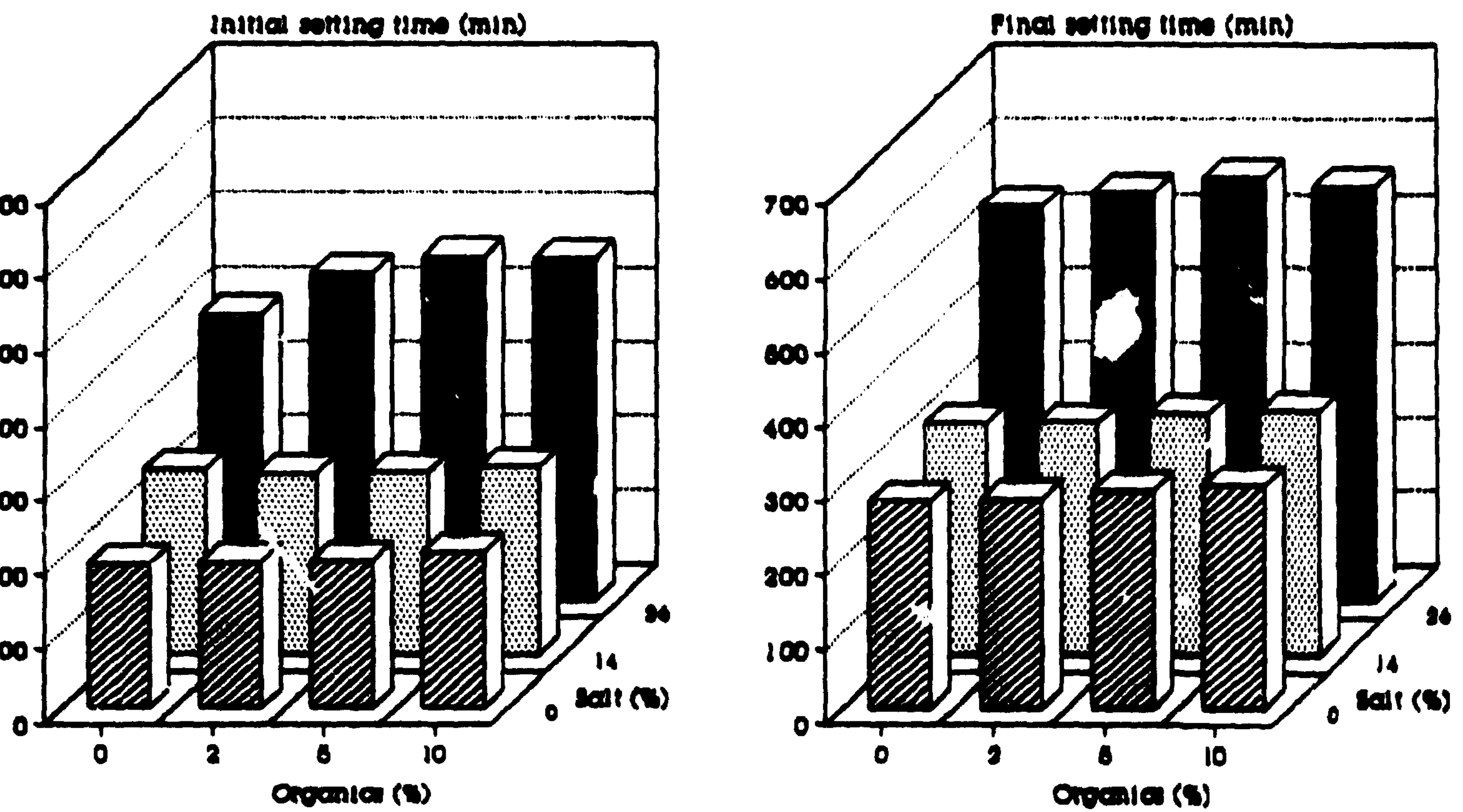

Figure 2 - Initial and final setting time for pastes with W/C = 0.30 and different $NaNO_3$ and TBP/DOD loads

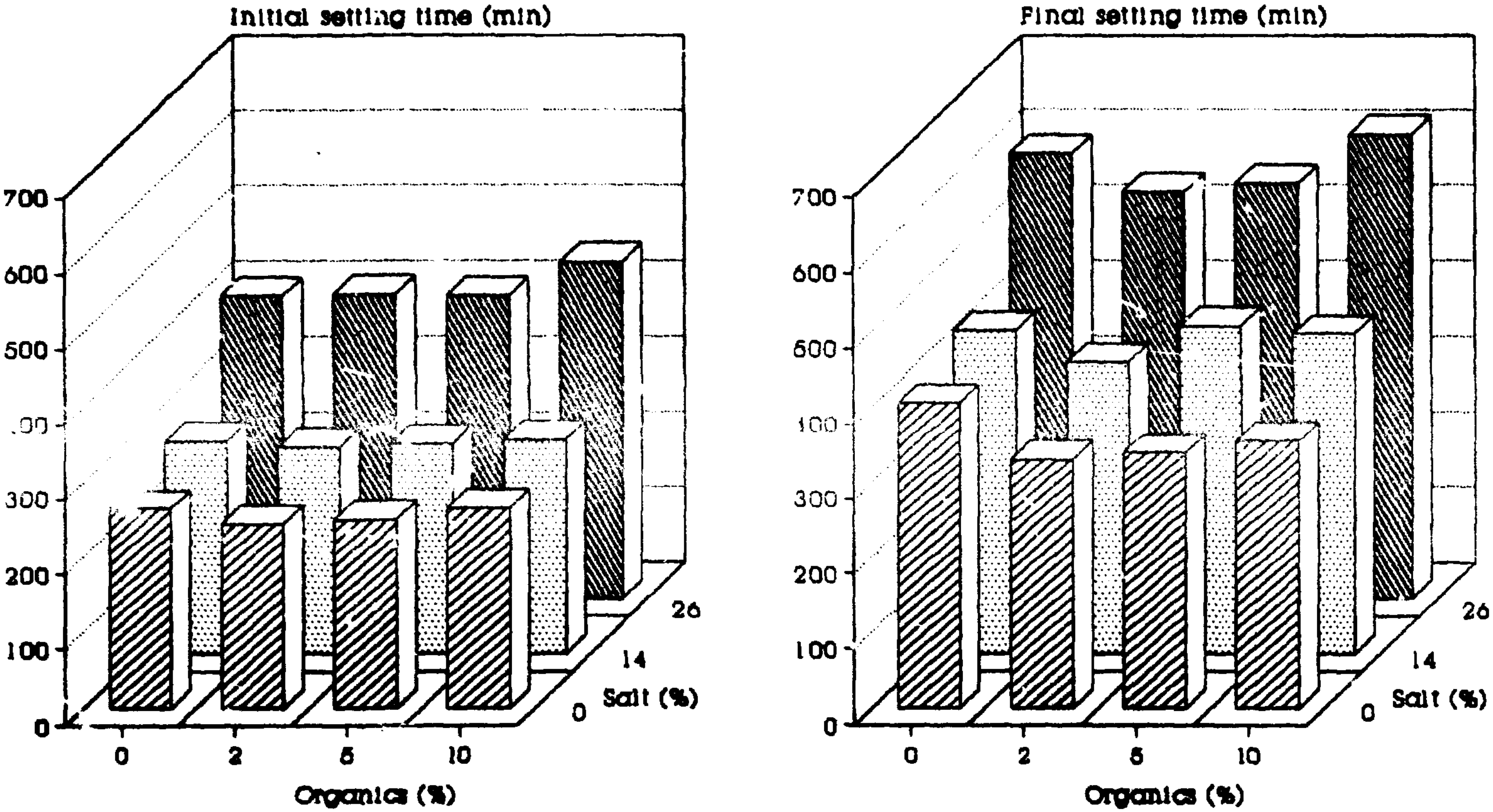

Figure 3 - Initial and final setting time for pastes with W/C = 0.40 and different $NaNO_3$ and TBP/DOD loads

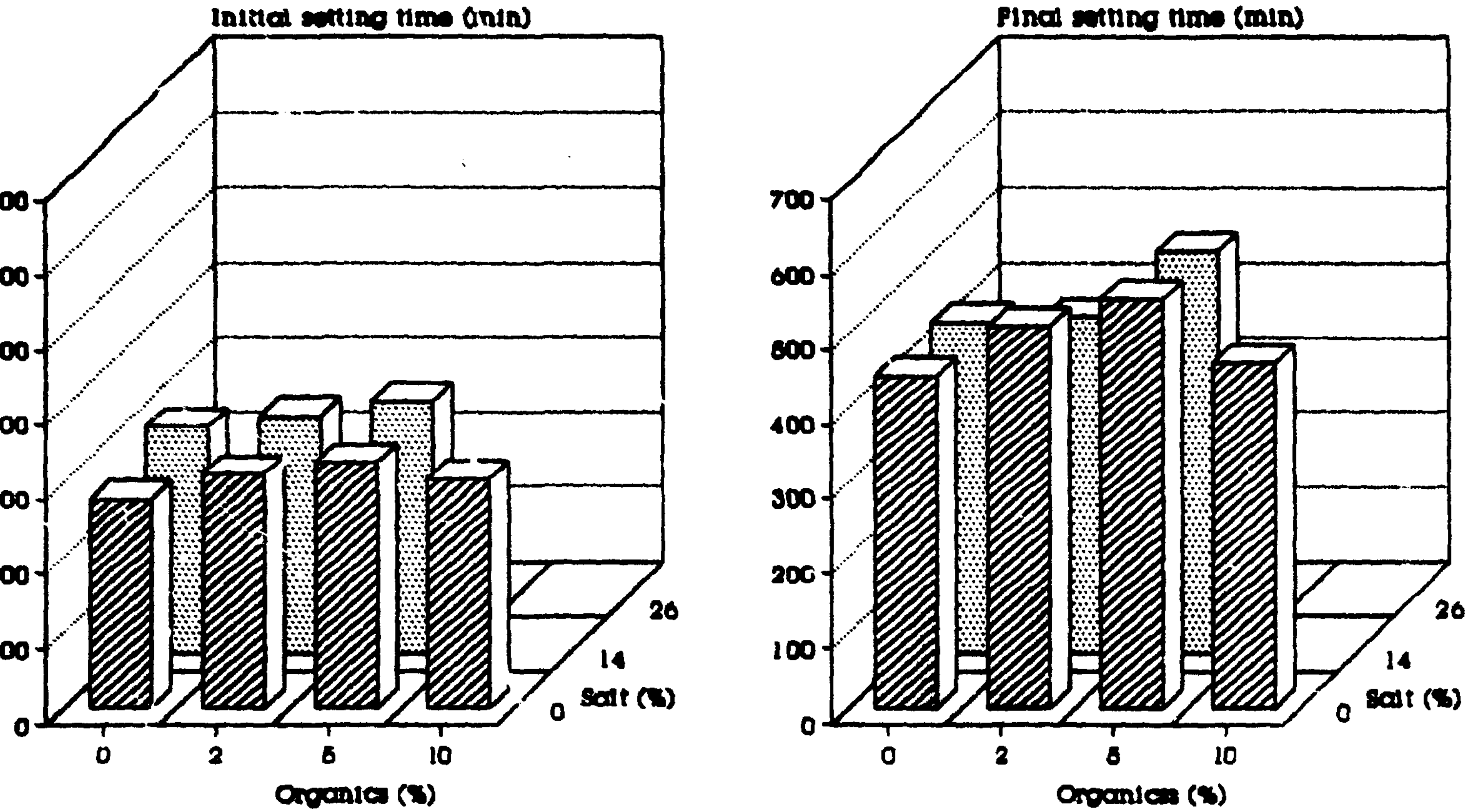

Figure 4 - Initial and final setting time for pastes with W/C = 0.50 and different $NaNO_3$ and TBP/DOD loads

assayed specimens presented fissures or cracks after the flame test.

Porosity and water absorption were determined in specimens molded in sealed cylindrical molds of 71 mm diameter and 71 mm height and cured at room temperature for 28 days. The porosity was determined through the measurement of the volume percentage of permeable pore spaces (voids) as described elsewhere (2). The observed porosity for specimens with organics are not so different from those where no organics was used as can be observed from the Figures 5, 6 and 7. The water absorption tests were done according the standard ABNT NBR 9778 (3). The water temperature was kept within 21 ± 2 °C and the immersion time was enough for the mass stabilization achievement in each sample. The obtained results show that the influence of the organics is not negligible as can be observed in Table II.

The organic phase was not segregated from the solidified matrix when the waste specimens were placed over an absorbent paper and subjected to vibratory shock testing simulating transport conditions. A vibrating table was used for that purpose during one hour period.

Mechanical strength was determined through compression tests on specimens of 50 mm diameter and 100 mm height.

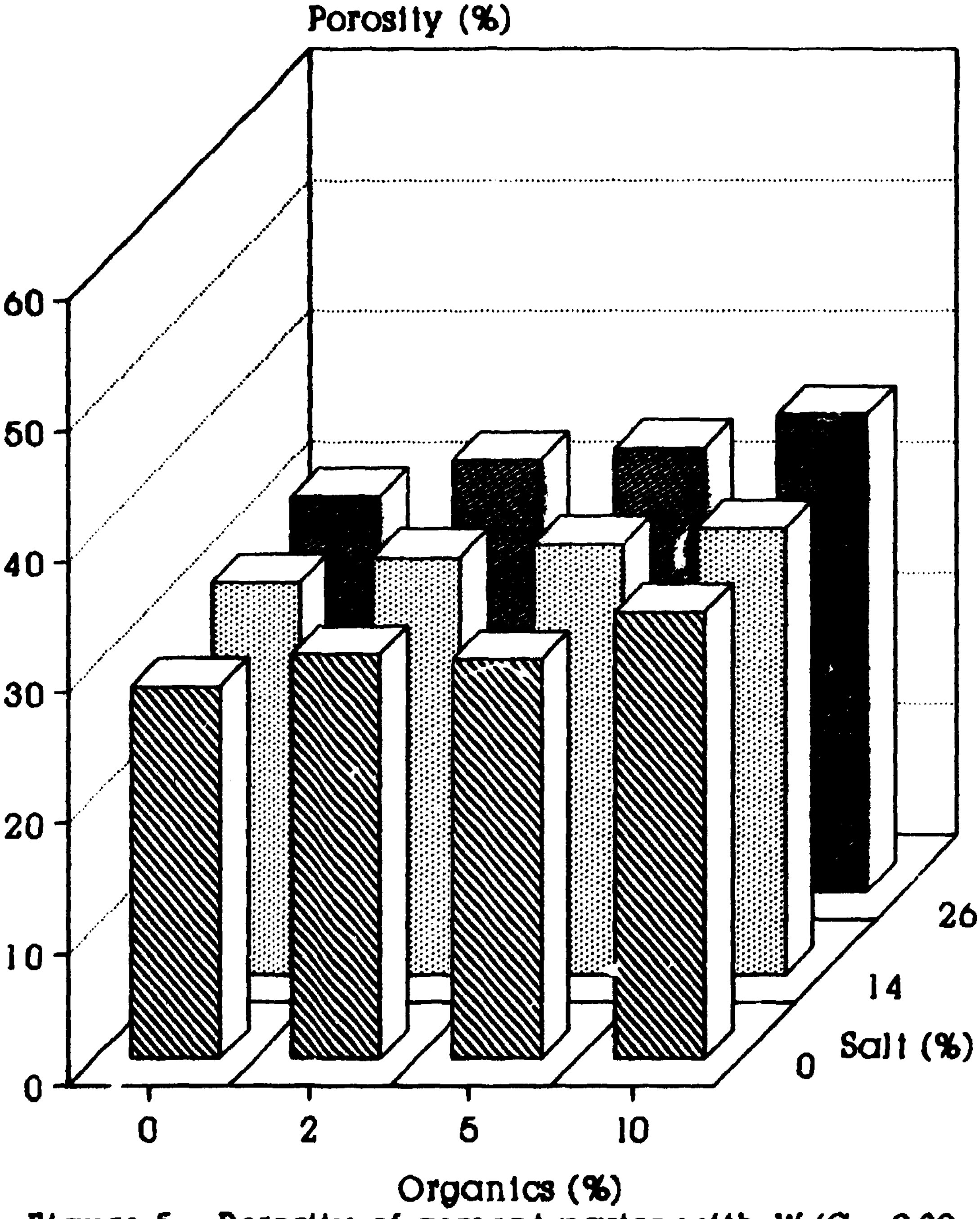

Figure 5 - Porosity of cement pastes with W/C = 0.30 and different $NaNO_3$ and TBP/DOD loads

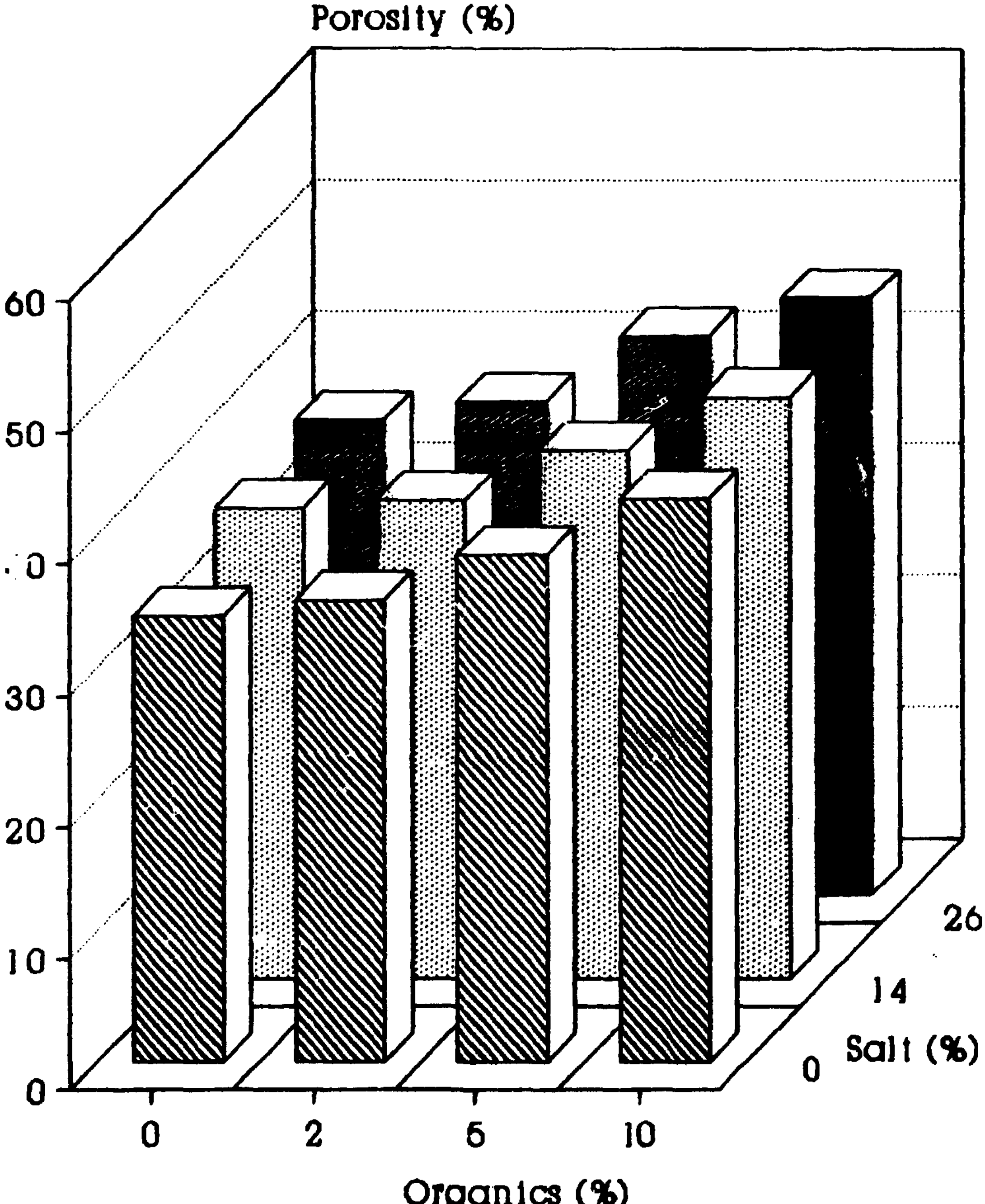

Figure 6 - Porosity of cement pastes with W/C = 0.40 and different $NaNO_3$ and TBP/DOD loads

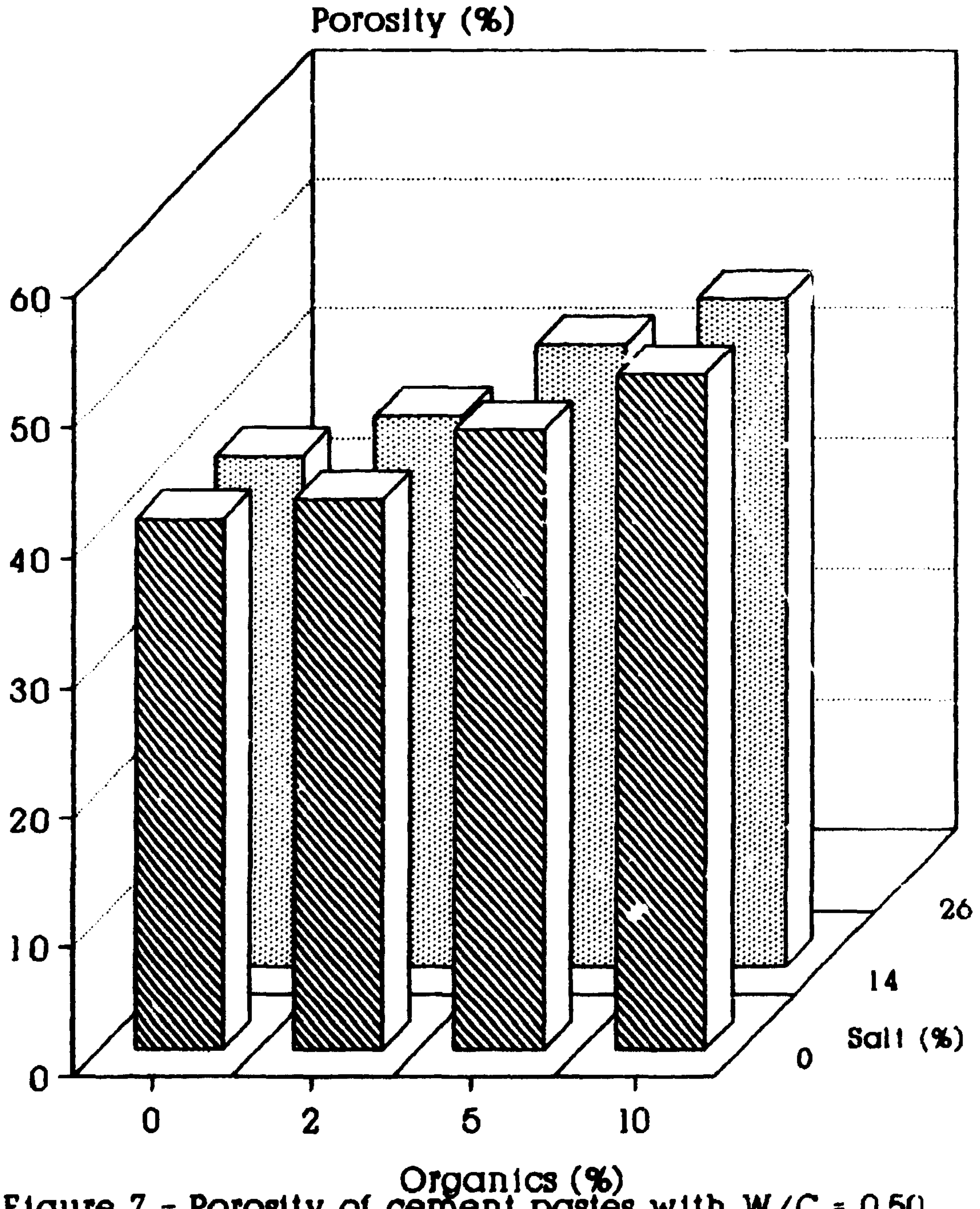

Figure 7 - Porosity of cement pastes with W/C = 0.50 and different $NaNO_3$ and TBP/DOD loads

Table II - Percentage of absorbed water in specimens containing sodium nitrate and TBP/DOD.

		W/C = 0.30	W/C = 0.40	W/C = 0.50
$NaNO_3$ (wt %)	TBP/DOD (wt %)	Water (wt %)	Water (wt %)	Water (wt %)
0	0	13.1	16.9	20.9
	2	14.2	17.7	21.7
	5	14.2	19.2	24.5
	10	16.3	21.9	26.6
14	0	14.5	17.7	20.1
	2	14.7	18.0	21.7
	5	15.3	20.1	24.6
	10	17.0	22.6	26.5
26	0	16.3	17.9	20.2
	2	15.2	18.6	22.0
	5	15.8	21.2	25.5
	10	17.5	22.6	27.5

After 28 days of sealed curing, the samples were capped on both tops and submitted to compression. The obtained results for different salt and organic content is shown in Figures 8, 9 and 10. The increase of mechanical strength with time was also observed for specimens with water/cement ratio equal to 0.40, 14 wt % of sodium nitrate and 5 wt % of TBP/DOD. This time dependent strength is shown in Figure 11.

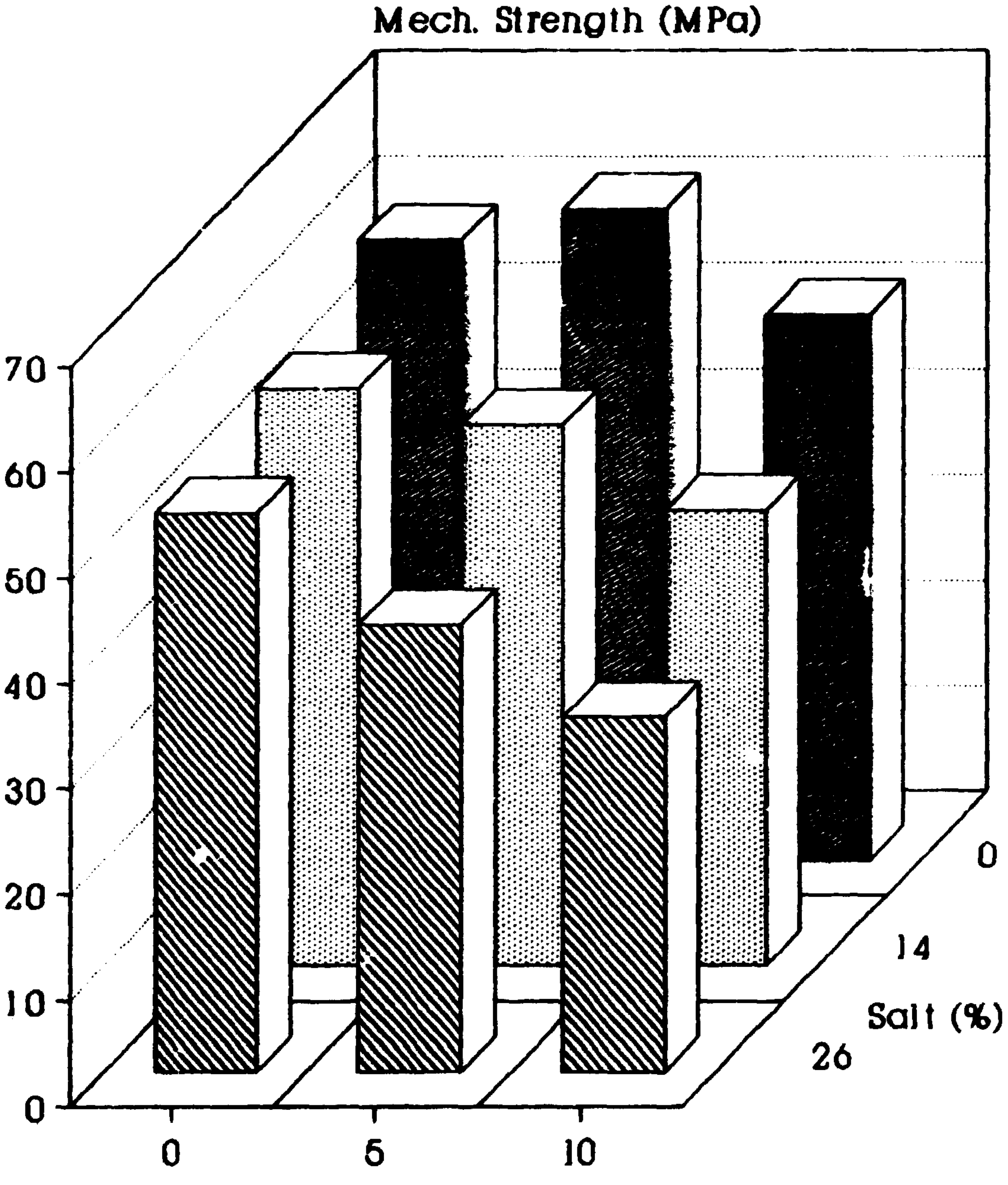

Figure 8 - Mechanical strength of cement pastes, after 28 d, with W/C = 0.30 and different $NaNO_3$ and TBP/DOD loads

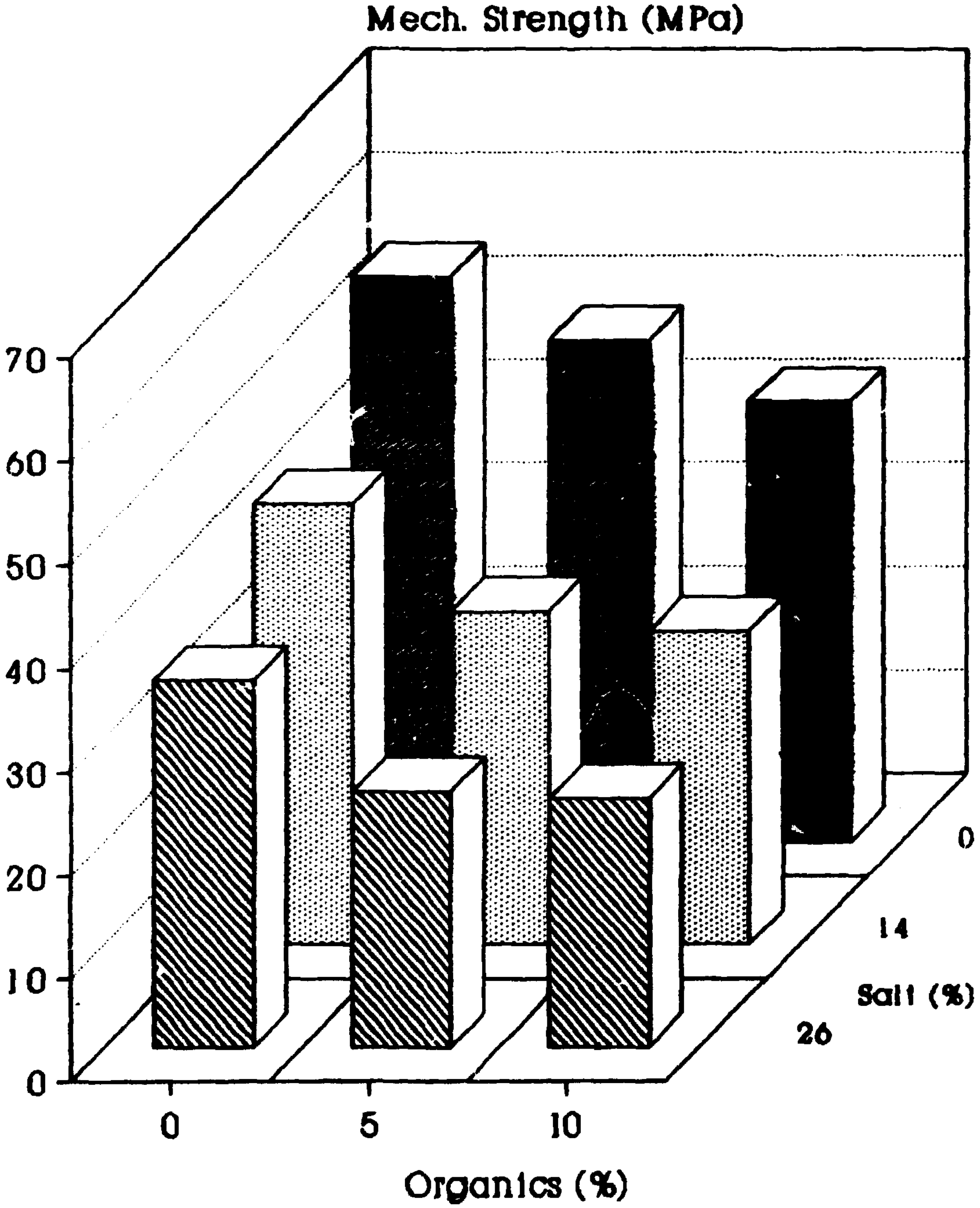

Figure 9 - Mechanical strength of cement pastes, after 28 d, with W/C = 0.40 and different $NaNO_3$ and TBP/DOD loads

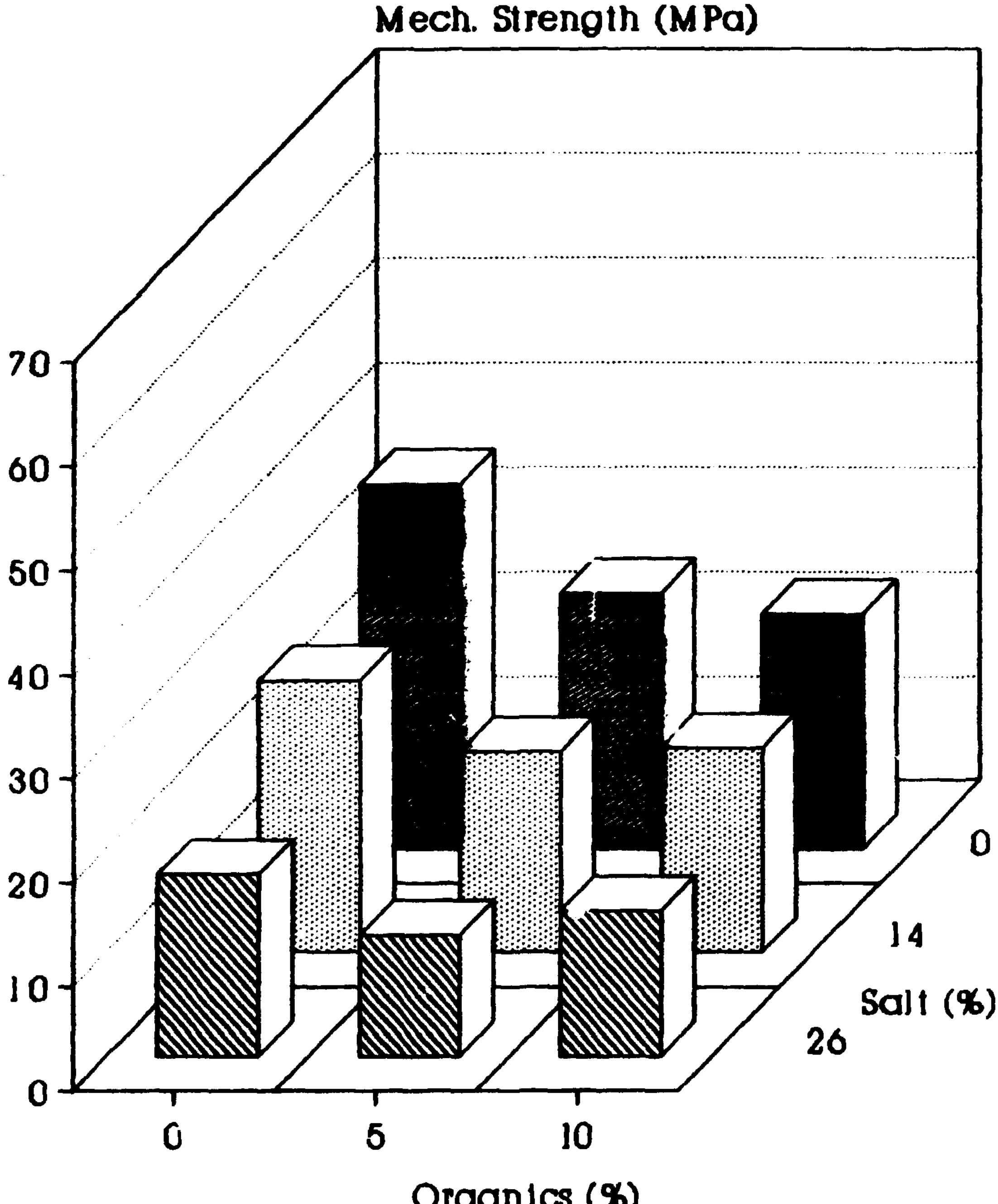

Figure 10- Mechanical strength of cement pastes, after 28 d, with W/C = 0.50 and different $NaNO_3$ and TBP/DOD loads

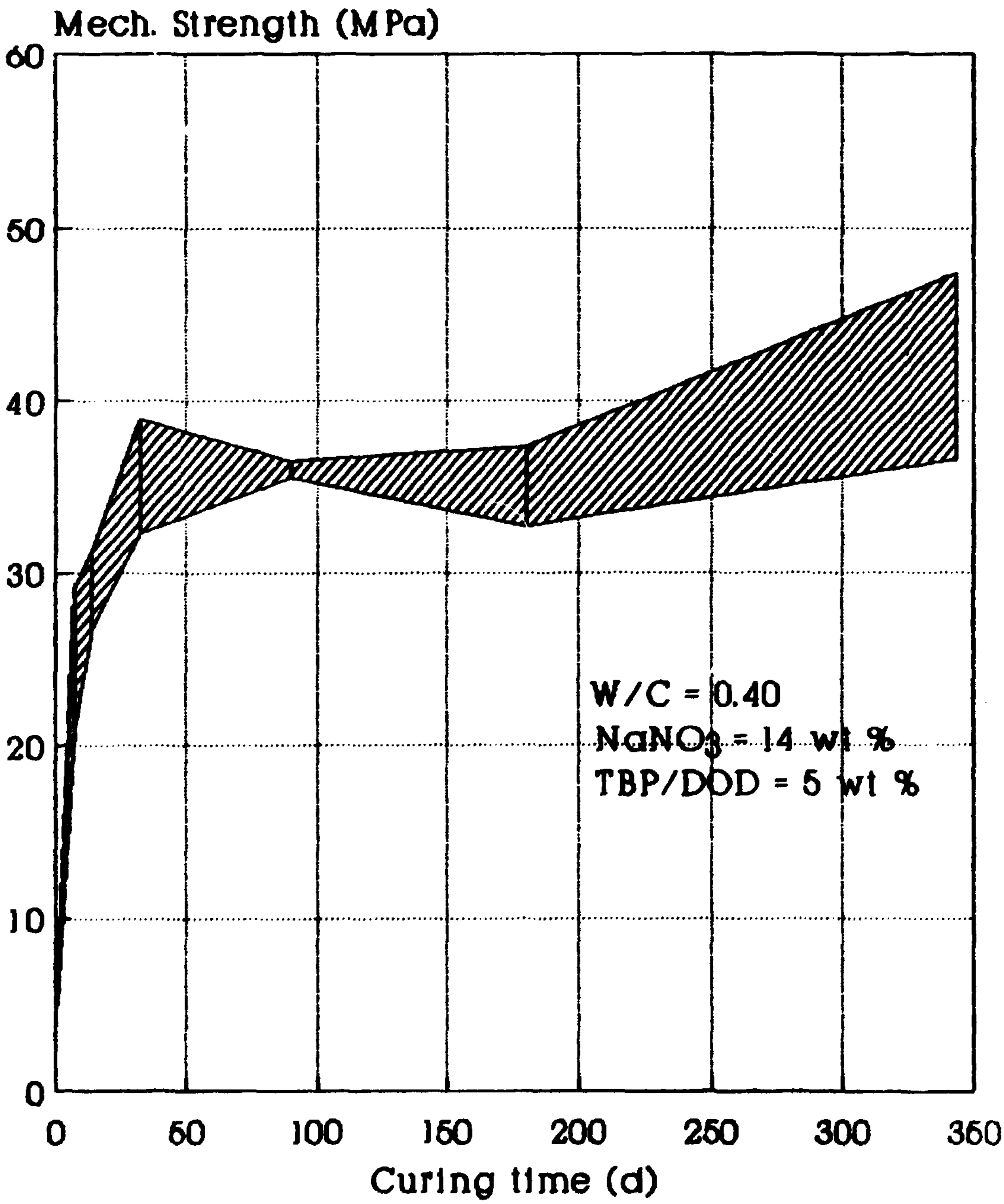

Figure 11 - Mechanical strength for the cement paste versus the curing time

CONCLUSIONS

It was observed that organic loads up to 10 wt % of the waste stream can be immobilized without using emulsifiers. The dispersion of the organic phase was sufficient to produce homogeneous mixtures with the cement. The results compares with those obtained elsewhere (1).

It is recommended that the water to cement ratio be kept lower as much as possible in order to provide a lower porosity for the final full waste form. This procedure will certainly improve the general properties of the waste form, such as the leaching rate, mechanical strength etc.

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