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ABSTRACT

The immobilization of nitric waste streams with ordinary Portland cement can be improved by use of some admixtures. The aim of this work was to investigate how the main characteristics of waste forms prepared with Portland cement pastes are modified by the addition of sulphonic naphthalene acids, lignosulphonic acids and emulsified fatty acids, which are present in some commercial admixtures. The effectiveness of the admixture in reducing the pore volume, as well as improving other parameters, depends on its chemical composition and on the amount utilized as well as the water to cement ratio and salt content. The admixture which has emulsified fatty acids in its composition shows some adverse results when the samples are immersed in water. The mechanical strength however is somewhat increased even when water load is increased.

CARACTERÍSTICAS DE REJEITOS IMOBILIZADOS MELHORADAS PELO USO DE ADITIVOS

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RESUMO

A imobilização de fluxos de rejeitos nítricos em cimento Portland comum pode ser melhorada pelo uso de alguns aditivos. O objetivo deste trabalho foi de investigar como as características principais de rejeitos imobilizados, preparados a partir de pastas de cimento Portland comum, são modificadas pela adição de ácidos naftaleno sulfônicos, ácidos lignosulfônicos e ácidos graxos emulsificados, presentes em alguns aditivos comercializados. A eficácia dos aditivos em diminuir o volume de poros, bem como melhorar outros parâmetros, depende da sua composição química e da quantidade usada assim como da razão água-cimento e conteúdo de sais. Os aditivos que possuem ácidos graxos emulsificados, em sua composição básica, mostram resultados adversos quando as amostras são imersas em água. A resistência mecânica é maior mesmo quando a quantidade de água na mistura é aumentada.

INTRODUCTION

Nitric waste streams with relatively long lived radionuclides arising from research laboratories or decontamination processes are usually classified as low- or intermediate-level radwastes and immobilized using ordinary Portland cement as a binder material.

This work is a continuation of a research program on immobilization of nitric wastes with national cement, started some years ago, and aims to verify the advantages or limitations of commercially available admixtures to improve the final characteristics of the waste form. It is well known that some amelioration on the end-product is attained as required for waste disposal. One of the most important improvements is to increase the workability of the paste promoting a better homogeneity of the product, reducing the porosity and increasing the integrity of the matrix.

It is well known that in cement pastes when the water load is increased the resulting solidified form has its permeability increased by capillary pore growth. This effect can be harmful when radwastes are immobilized, since the main transfer mechanism of radionuclides to the biosphere is through water movement between the waste form and the repository.

The Brazilian concept for low- and intermediate-level waste disposal, that is, near ground surface repository, requires that the engineered barriers in terms of waste forms be as good as possible in order to guarantee its long life. Moreover, these should provide safety during transportation and emplacement.

Low water to cement ratio is desirable in order to increase the mechanical strength of the waste form.

Consequently its workability decreases making necessary great power to produce a uniform paste. This problem could be solved by using chemical admixtures that produce workability. However, the application of admixtures, commercially available or not, depends upon many factors, including curing and properties of all individual materials and their proportions. The choice of a specific admixture should be done only after some experimental work has been completed.

Based on all those considerations, three kinds of commercial admixtures were studied experimentally: a water reducing agent composed of a lignosulphonic acid, a superfluidifying compound based on naphthalene sulphonic acid and a sealant whose main component is an emulsified fatty acid. Their trade names are CEMIX, ADIMENT and VEDACIT respectively.

Physical properties of the end-product were explored in order to analyze the viability of the admixture use in nitric wastes cement conditioning practices. The aim is to get better micro-structural and physical-chemical properties that result in a guarantee of the final durability of the cement forms.

EXPERIMENTAL PROCEDURES

Pastes were prepared with ordinary Portland cement produced in Brazil, with its chemical composition given in Table I, and sodium nitrate to simulate nitric waste streams. Hydrated cement mixtures with water to cement ratio, (W/C), equal to 0.30 and 0.40 were assayed. Sodium nitrate was used as 3.6 and 7.5 % by weight. All combinations were prepared and cured in sealed vials at room temperature.

Table I - Utilized cement composition

Compound	Total amount (wt %)
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

To test each admixture, all formulations were prepared using the manufacturer's maximum recommended proportions and their half values. The proportions were based on the cement contents. To observe their influence on waste immobilization, samples without admixtures were tested also. Table II gives the main characteristics of the admixtures used.

Table II - Admixtures assayed

Trade Name	Density (gcm^{-3})	Recommended proportion (a)
ADIMENT	1.12	1.5
CEMIX	1.20	0.2
VEDACIT	1.00	1.0

(a) percent on weight of cement

Because of the difficulty to use W/C = 0.25 in a normal immobilization process, this ratio was tested only for mechanical strength, by using the superfluidifying and water reducer agents.

Cement pastes with simulated radwastes and admixtures were prepared using a planetary paddle mixer. The resulting mixtures were poured inside specific molds for each kind of test. Four samples were prepared for each formulation tested.

The specimens were unmolded after 24 h and stored, at room temperature, during 28 days in airtight containers until ready for testing.

Homogeneity

The demonstration of homogeneity of samples prepared according the procedures used in this work was done by using the technique, described elsewhere (1), of measuring delayed neutrons produced by irradiation of samples containing natural uranium compounds as tracers.

Free standing water

Parts of the mixtures prepared for homogeneity tests were enclosed inside graduated and sealed tubes, and kept at room temperature for some period of time. It was seen that only one formulation, namely W/C = 0.40, $NaNO_3$ = 7.5 wt % and ADIMENT = 1.5 cement wt %, presented a thin film of free water after 24 h, detected by visual inspection and which disappeared after 48 h.

Integrity

The integrity of solidified cement forms can be observed when samples are immersed in demineralized water for a period of time. If water intrusion into the capillary interconnected pores does not disrupt the structure, the specimen will be considered as a free standing solid, i.e.

its macroscopic integrity is achieved, when it does not disintegrate under water immersion. Specimens were of cylindrical shape with 71 mm diameter and 71 mm height. The tests were performed after 28 days of sealed curing.

Setting

Setting time of pastes made of different formulations was evaluated by using a manual Vicat apparatus. Initial and final setting times were determined in fresh pastes under controlled room temperature.

Porosity

Porosity was determined through the percentage volume of permeable pore space (voids). The samples were prepared for W/C = 0.30 and 0.40 with different sodium nitrate loads and the maximum recommended proportion of admixtures. The specimens were molded in cylindrical molds of 71 mm diameter and 71 mm height and cured at room temperature for 28 days (2). The samples were unmolded and oven dried until the weight equilibrium was achieved. The specimens were then saturated with water by immersion. Dry and water saturated samples were weighed in air. Those water saturated were also weighed under immersion. The resulting values allowed the determination of the percentages of voids in hardened pastes.

Hydration temperature

Hydration temperature was determined during the first 24 h for specimens of 165 mm diameter and 180 mm height with the same procedures as described elsewhere (3).

Compression testing

Mechanical stability was determined through compression tests on specimens of 50 mm diameter and 100 mm height. After 28 days of sealed curing, the samples were capped on both ends and submitted to compression. Each result was obtained as an average of four tested samples.

RESULTS AND DISCUSSIONS

Homogeneity

From previous experiments (1), it has been verified that the addition of $NaNO_3$ to the paste results in better workability. This is so when the percentage of $NaNO_3$ is increased from 3 wt % to higher values, even for mixtures of W/C=0.30. This is specially true when a water reducer or a superfluidifying agent is used which makes the achievement of homogeneity rather easy, even for W/C=0.25.

In mixtures with the sealer agent, homogeneity is achieved throughout the nitrate addition and mixing actions.

Integrity

All prepared formulations which gave rise to monoliths were immersed in water for 36 days and shown to be free standing solids. No cracking nor swelling was observed in any group of specimens. As in other experiments that depend on water immersion (leaching, permeability etc), it was verified that water attacks the cementitious material.

Setting time

The results obtained for initial and final setting times are shown in Figures 1 and 2. Each result is the average of setting time values obtained for three samples with the same formulation. It was observed that the $NaNO_3$ delays the initial and final setting time and the use of admixtures affects the setting in different rates.

When the mixtures do not contain $NaNO_3$, the effect of admixtures is to accelerate the initial setting for W/C=0.30 and keeping somewhat the same values for W/C=0.40. While

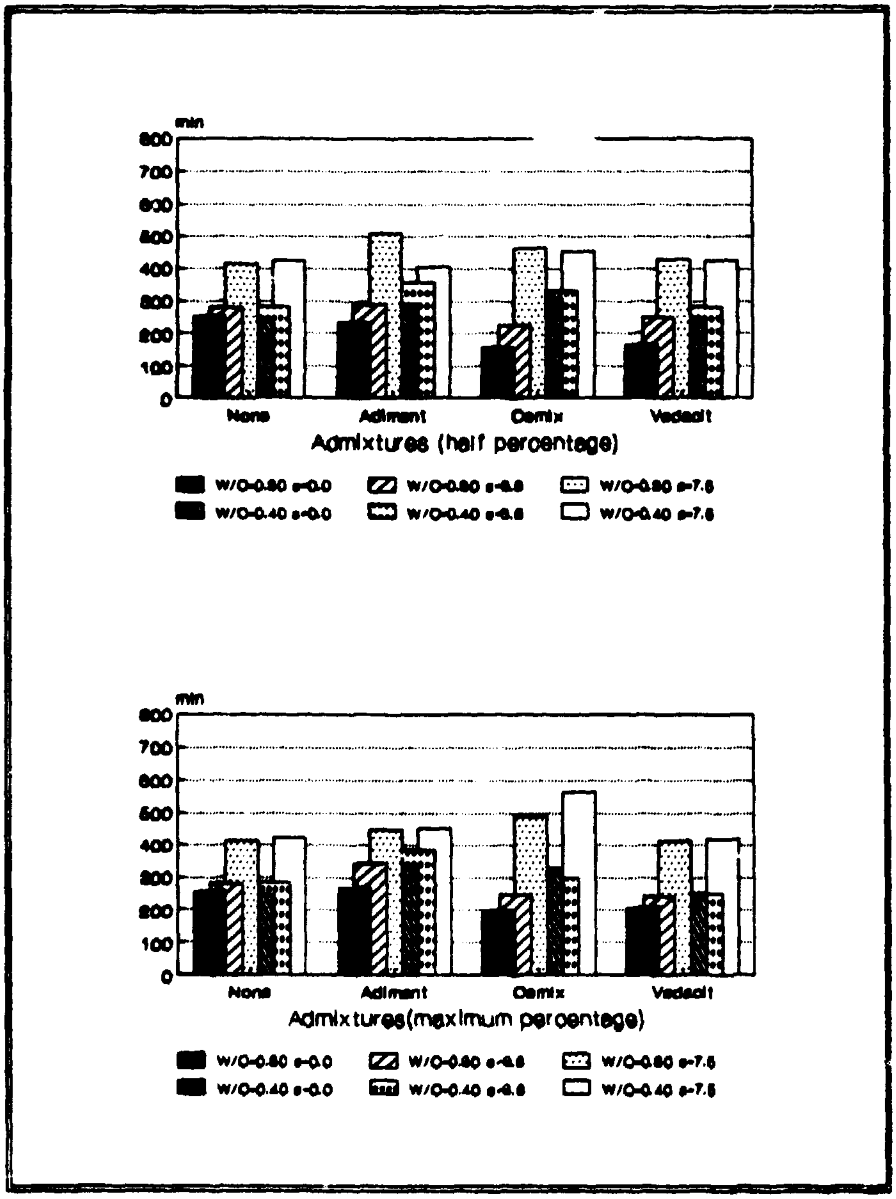

Figure 1 - Initial setting time of cement pastes for different W/C ratios, $NaNO_3$ contents and admixtures types

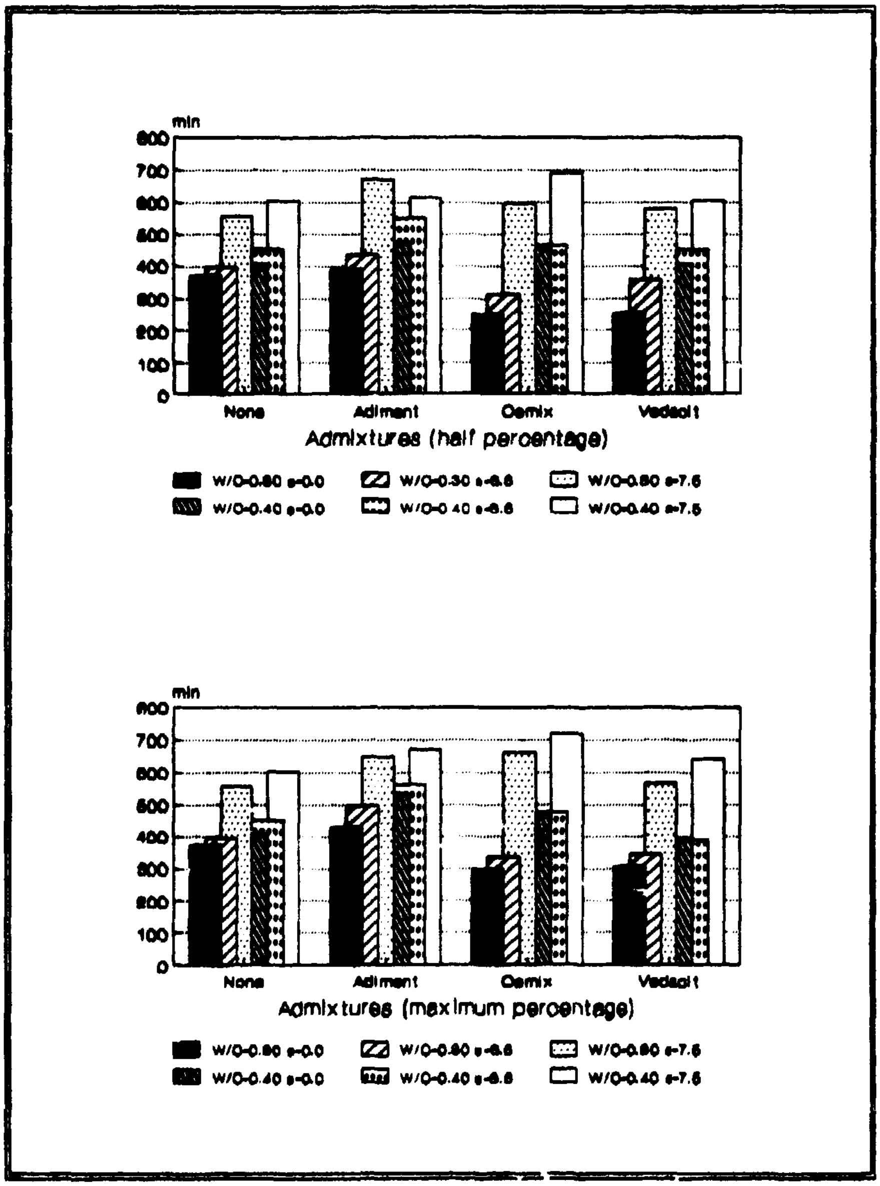

Figure 2 - Final setting time of cement pastes for different W/C ratios, $NaNO_3$ contents and admixtures types

salt content is increased a retardation process occurs. It can be seen that for W/C=0.40 and a maximum proportion of superfluidifying agent there is a delay in the initial setting of about 35%. This do not happens when a half proportion is used.

Final setting time also gets longer as $NaNO_3$ content increases. The influence of the use of admixtures is observed throughout the increment in the final setting time.

It is observed that the sealer does not change the setting time as much as the other two agents.

Porosity

Figure 3 shows the average results obtained with W/C equal to 0.30 and 0.40. As can be observed, the volume of connected pores is somewhat higher for $NaNO_3$ =3.6wt % and falls below those values when salt free samples without and with admixtures were tested. The only exception occurs with the superfluidifying agent. It can be seen that the use of the admixtures utilized in this work does not change sharply the values of the porosity which remains between 25 and 31 vol % for W/C=0.30 and between 32 and 39 vol % for W/C=0.40. The dispersion of the porosity values is around 22 % for both cases.

Hydration temperature

It has been observed (3) that when the load of $NaNO_3$ in the mixture increases, the temperature evolution is retarded and lowered by a factor of about 1.4 for W/C=0.30 and 1.6 for W/C=0.40. This occurs because the chemical reactions are retarded as salt content and water increase in the composition of the pastes.

When the sealer is introduced in the formulations, the changes in temperature evolution are not significant. If the

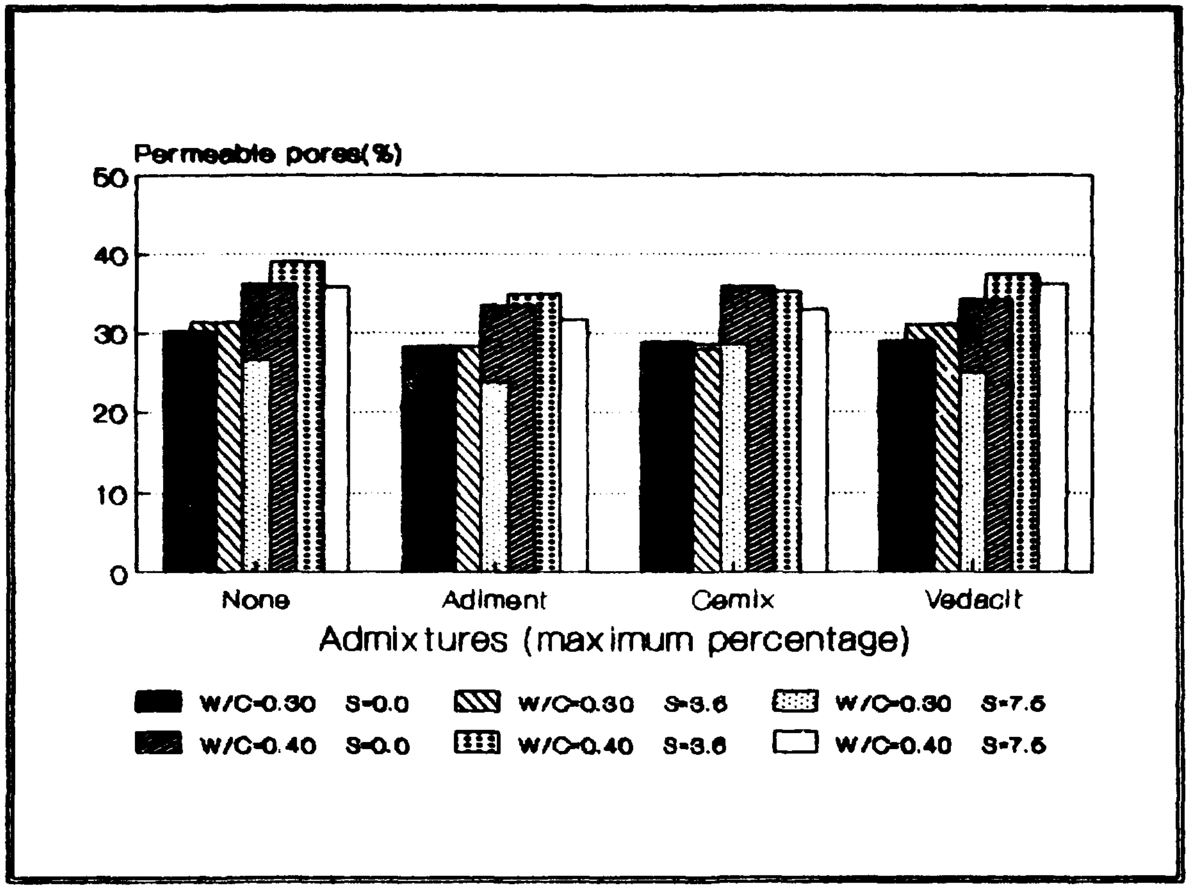

Figure 3 - Total volumetric percentage of permeable pores in cement pastes for W/C = 0.3 and 0.4, different salt contents and admixtures types

water reducer or a superfluidifying compounds are mixed, together with a larger amount of $NaNO_3$, the hydration temperature is lowered about 30 % and retarded about 25 %.

Compression testing

The use of admixtures for cement conditioning of neutralized nitric wastes can improve some of the characteristics of the final waste form.

It was thought that the use of an emulsified fatty acid could be useful to diminish the permeability of cementitious specimens as it is normally used as an impermeabilizing product. However, the presence of sodium nitrate in the formulations modifies their chemical behavior but not the mechanical strength when the water load is diminished from 0.40 to 0.30. This fact must be further explored by combining the admixtures.

The water reducer and superfluidifying compounds are shown to be effective even when the salt content varies from 3.6 to 7.5 wt %. It is somewhat difficult to fix the best admixture load, because no aberrant results were observed when the water, salt or admixtures proportions were varied, in any of the formulations used in this study. The results are shown in Figures 4,5 and 6.

Other tests should be made in order to explain, in more detail, the influence of the waste content together with the admixtures on the chemical processes which occur in the cement matrix.

Efforts are in progress to perform the necessary quality control of the incoming compounds and to determine the advantages of using the various admixtures with respect to other parameters, i.e. leach rates of the solidified products as well as corrosion resistance.

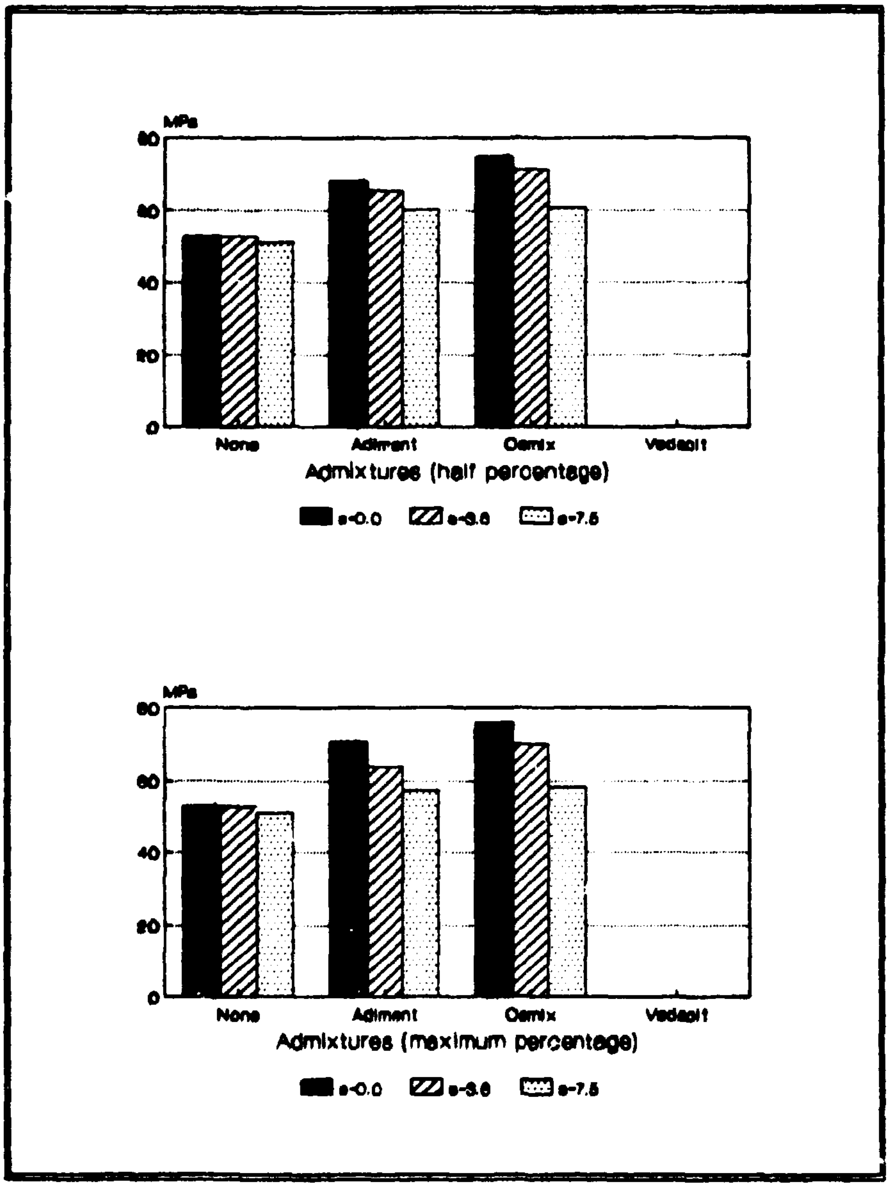

Figure 4 - Compressive strength of cement pastes with W/C = 0.25, different $NaNO_3$ contents and admixtures

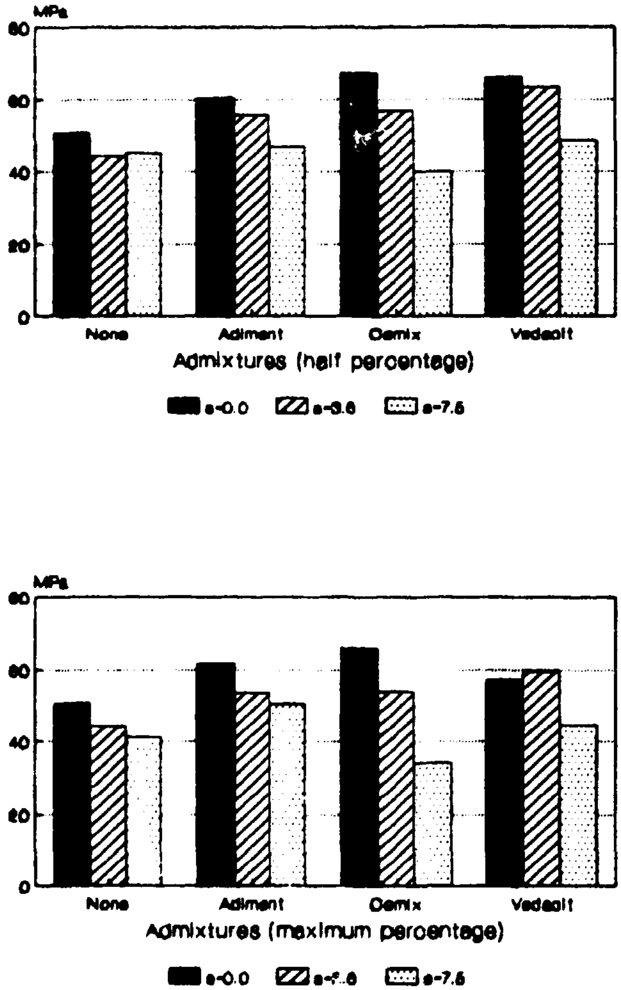

Figure 5 - Compressive strength of cement pastes with W/C = 0.30, different $NaNO_3$ contents and admixtures

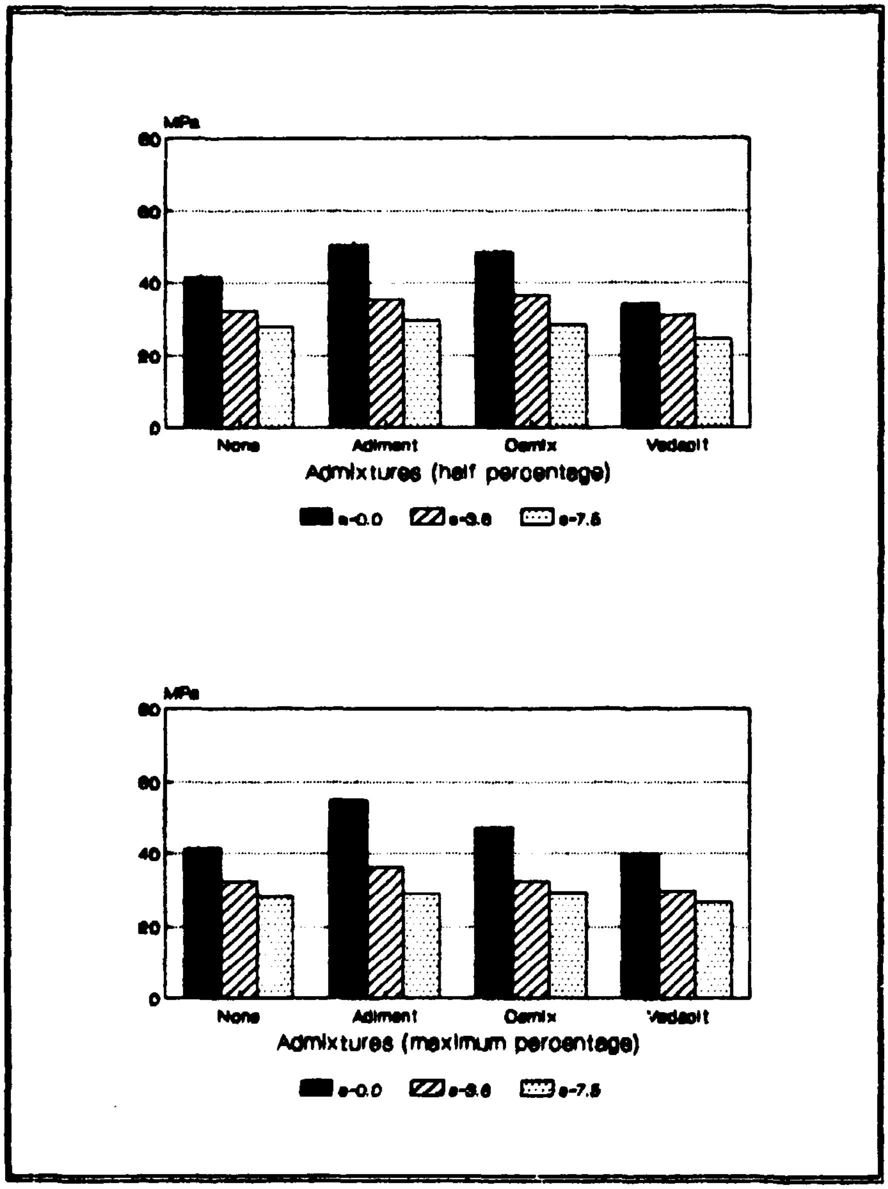

Figure 6 - Compressive strength of cement pastes with W/C = 0.40, different $NaNO_3$ contents and admixtures

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