ON-LINE, NONDESTRUCTIVE METHODS FOR COMPRESSIVE STRENGTH PREDICTION IN WASTE CEMENTATION

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ABSTRACT

The ability of nondestructive evaluation techniques to predict the long term compressive strength of waste forms during their processing was evaluated through experiment. It was determined that the compressive strength and mixture consistency were predictable through analysis of the rheological properties of the paste during mixing, and through monitoring of the early maturity development during curing. Ultrasonic methods were shown to be less applicable.

INTRODUCTION

The control of product quality during processing is preferable to verification just before storage because of its higher reliability, traceability, and adaptiveness to corrective action. Three tests which may be appropriate for use in an on-line quality control application involving cement include maturity analysis, rheological analysis, and ultrasonic pulse velocity analysis. An experiment has been designed to evaluate the three tests on their sensitivity, reproducability, and reliability in monitoring changes in mix consistency and in predicting short term (seven day) compressive strength development.

THEORY

The experiment relies on Gaussian statistics and correlation theory to evaluate the relationship between a given, measurable (at an early stage) quantity and the compressive strength after a seven day curing period. In order to prove that control of product strength is possible, a relationship must be developed between the strength and a measured quantity, such as maturity after six hours of curing.

The Linear least squares equations are used to correlate all variables in this report. The correlation coefficient, r, is used to define confidence levels.

Ensuring strength control during the mixing of the cement can theoretically be accomplished by analyzing the rheology of the cement paste, as done in the literature (1). Since cement is not a Newtonian liquid (it is a suspension of particles which are chemically reacting), use of traditional viscometry equipment is precluded. Several methods for measuring the torque of the mixer have been identified and include strain gauges, electric power consumption, hydraulic oil pressure measurement, and optical torque transducers (2). Because of available equipment, electric power consumption was chosen for this study.

Once the power or torque to drive the shaft a certain velocity has been measured, characteristic curves can be developed which can be used to ensure consistency. Analyzing the shape of and numerical values given by the curves provides information about the strength of the waste form.

During the curing of the waste form, measurements can be taken of the temperature development of the form with time. Integrating the resulting function, and multiplying by a cement correction factor ("C" value) results in a quantity termed maturity. The equation for maturity used was (3):

$$R = \Sigma_i(t_i T C^n) \qquad \text{(Eq. 1)}$$

where:

R = the maturity at the time,
t = the width of the temp. step (5°C),
T = the time (hr) that the cement temp was, in a particular temp. step t_i, starting with -10 centigrade,
C = the cement factor ("C" value),
and n = an exponent, defined for each temp. step.

The Maturity was calculated by the thermocouple computers used. The "C" values were provided by the cement manufacturer (1.25 for OPC and 1.50 for the slag cement).

The relationship between maturity and strength at a given time has been well established, and is in common use, especially in Europe, for nondestructive evaluation. It should be noted, however, that this particular experiment is attempting to relate the maturity in the early stages of curing to the strength at some later time (specifically seven days).

The development of the ultrasonic pulse velocity with time is worth investigation. In the early stages of curing, while the cement is still a paste, the impedance to the ultrasonic pulse is caused by the inability of the particles to roll over each other, so what is actually being measured is some type of viscosity related property. Once the onset of setting occurs and part of the cement has solidified (the top layer crusts over), the impedance to the ultrasonic pulse is caused by molecular vibrations, as in other solids.

The observed pulse velocity through a solid is related to the elastic modulus, and thus the compressive strength, through the relation:

$$v^2 = AE/\rho \qquad \text{(Eq. 2)}$$

where:

v is the observed velocity,
A is a proportionality constant,
E is the elastic modulus,
and ρ is the density of the solid.

The pulse velocity observed should steadily increase as the strength of the cement rapidly increases during the early stages of setting.

EXPERIMENTAL METHOD

In order to guarantee that the results of the tests were consistent over a wide range of dynamic situations, several conditions were imposed on the testing of the waste forms. Included in the tests were the following phenomena, some inherently present, others purposely instituted:

1. sensitivity to the operator (experience, new personnel, pressure applied, ...)

2. amount of day-to-day consistency achievable,
3. the use of OPC or OPC/slag cements,
4. waste enrichment (low vs. high),
5. small (ten percent or less) changes in waste enrichment,
6. small water to cement (w/c) ratio changes,
7. changes in mixing time, and
8. changes in cement addition rate.

All of the changes were implemented before or during the mixing of the cement. Changes were avoided during curing to help ensure that any relation between measured quantities and seven day strength would not be disturbed as the waste form cured.

The waste forms that were tested were in the form of 15 cm. square cubes that were individually prepared. The amount prepared was 7.7 kg., and the cube's mass was around 6.5 kg. The difference was prepared to avoid scraping the mixing container out after each run (deemed a cause of inconsistency).

Data on the composition of waste forms tested is given in Table I. HOC-A is a blast furnace slag cement and OPC is Ordinary Portland Cement. The waste forms mimic those manufactured at the Dodewaard BWR in the Netherlands. Previous studies at KEMA (4,5) have identified the proportions needed to achieve ideal consistency.

Out of twelve to thirteen samples produced each week, approximately eight were prepared using the compositions given in Table I. These samples were used to statistically analyze the data. In the interest of observing the dynamics of the given tests to small variations in the waste form constitution, the remaining samples were prepared with slight deviations of components (a little too much or little waste, small changes in water/cement ratio, ...). The information obtained from these samples was used in a qualitative sense to observe the effect these changes had on test results.

TABLE I

Composition of Waste Forms Used (mass %)

Component	Waste Form 1	Waste Form 2	Waste Form 3
cement	OPC 66.0	OPC 60.0	HOC-A 65.2
anion exch. resin	0.952	4.72	0.942
cation exch. resin	1.13	5.63	1.13
precoat	3.14	3.11	3.11
brine	28.8	26.5	29.6

RESULTS

General Comments

The cemented waste forms were examined during the pouring of cubics and after destructive testing. It appeared that the waste was homogeneously distributed throughout the cubes in all cases. This was true even in samples which contained purposely higher water to cement ratios. It was necessary to only visually inspect the samples, as mix quality was not a major goal of the study. Any clumping or settling of contents was, however, deemed to be a possible cause of strength inconsistency. Settling would also be a major problem in the real world waste processing, as it would result in higher radionuclide activity and altered physicochemical properties in the base of the container.

The viscosity is, for purposes of this research, related to the consistency, and the terms will be used interchangeably. The slag cement used (HOC-A, greater than 65% slag) absorbed the water very quickly (higher blaine or fineness), and was difficult to mix with the constructed mixing system and procedure. The water to cement ratio was therefore raised from 0.436 to 0.453 in order to obtain a consistency similar to (OPC) samples.

The three tests relied on comparison of measured values to the seven day compressive strengths obtained on a Seidner form tester. The strengths obtained for the given batch's control samples is shown in Table II.

The high deviation and range exhibited by the first batch is evidence of the effect of operator experience on the system. The decreased sample base in the second and third batches reflects the desire to obtain more samples with minor deviations.

Rheology Analysis

The electrical power consumed and corresponding torque (power/rotational speed) were analyzed as functions of the velocity of the mixer's shaft. The generated information resulted in a method which is very good at determining sensitivity to changes in mix, such as water to cement ratio.

The plots of torque versus velocity did not appear to be linear, such as those obtained in the past (1,6). The plots generated here were similar to a 1/x function. Because of the lack of a linear torque/velocity function, an apparent viscosity could not be defined for the waste forms, as Tattersall had done.

Although the torque/velocity plots were hard to interpret (and have therefore been omitted from the report), the

TABLE II

Seven Day Strengths of Control Samples

Batch Description	Number of Samples	Ave. Strength (N/mm^2)	Max. Strength (N/mm^2)	Min. Strength (N/mm^2)	Standard Deviation (%)
OPC/4% waste	10	46.1	48.0	41.3	5.73
OPC/12% waste	7	26.2	27.7	25.2	3.24
HOC-A/4% waste	7	45.8	47.9	44.4	3.40

rheology analysis of the mixing process did yield interesting results. Plots generated of the motor's power consumption as functions of the velocity for each sample were generated. The resulting plots are shown in Figs. 1, 2, and 3 for the three types of waste forms tested. These plots show the power consumed by the motor for some of the control samples (including the most deviant 'max' and 'min' samples), for an 'average' control sample, and for all other samples (those with varying water content, waste content, or mixing time).

Figure 1 shows the power/speed relationships for the samples containing OPC with normal (4%) waste content. A distinct area is created within which the control samples fall. This 'control area' is considerably wider at higher velocities, which means that the lower speeds may be more sensitive to mixture variations. The two lowest curves are those corresponding to high water to cement ratio (0.5 instead of 0.436), or too much waste (double). They fall clearly out of the control area. The other curve that is low occurs from a control sample that had an unexplainably thin mix. The mix was visibly thinner, and yet the strength obtained seemed normal. The existence of such a sample bodes poorly for the usefulness of this test in process control situations.

The samples containing OPC with high (12%) waste content are plotted on Fig. 2. In order to assess the sensitivity of the tests, it was decided to test more samples with deviations, concentrating on water to cement ratio changes. The plot shows a much tighter control area when compared to the previous plot. This difference has been assessed to greater standardization in procedure resulting from increased operator experience. Comparison of the deviant curves to the control curves shows that the test is very sensitive to changes in water to cement ratio. The sample containing two percent too high a w/c ratio (0.450 compared to 0.441) lies at the approximate resolution limit of the test. One very interesting result is that the samples containing too little or too much waste contradict findings from the previous (OPC/4%) samples. That is, the deviant samples containing too much waste were thinner than the controls. This fact implies that there is a waste enrichment between four and twelve percent which will result in a maximum slump. It is easy to see how this has major implications on the proportioning of mixture ingredients in the processing of the waste.

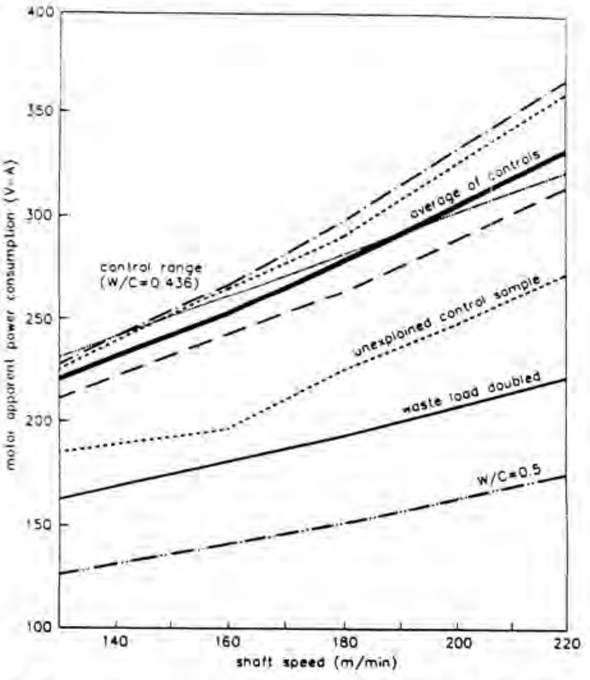

Fig. 1. Power versus velocity for batch 1 (OPC with 4% waste).

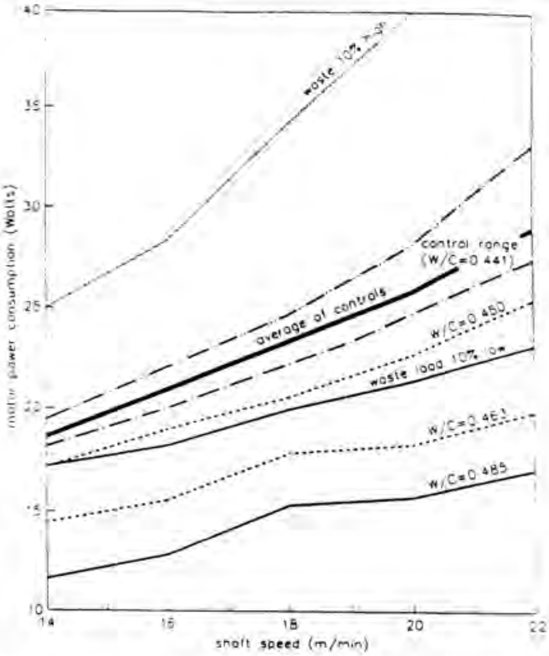

Fig. 2. Power versus velocity for batch 2 (OPC with 12% waste).

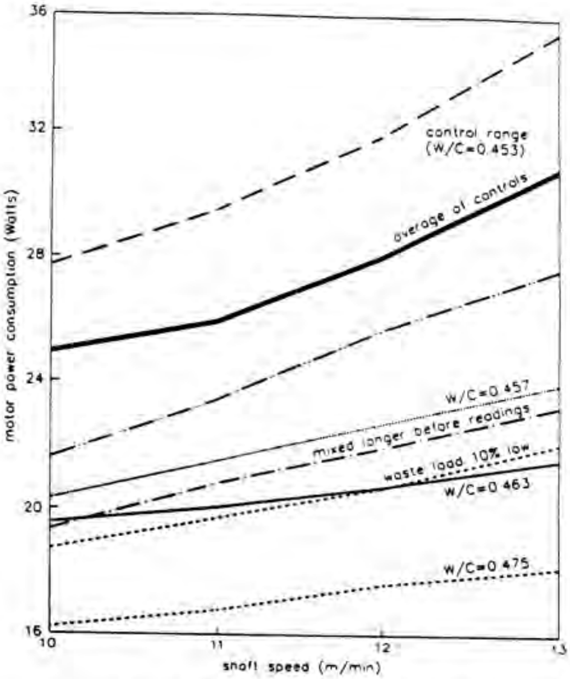

Fig. 3. Power versus velocity for batch 3 (HOC with 4% waste).

Figure 3 shows similar results that were generated for the slag cement. This figure shows a wider spread of control samples than the previous figures. This fact can be explained by the higher blaine of the slag cement (450 compared to 280 m^2/kg), which causes the water to be quickly absorbed and causing a thicker mix. This thicker mix forced the velocities at which the power measurements were taken to be lowered as seen on the abscissa. Similar sensitivity to water content was found as in the previous batches, and the sample containing ten percent less waste was thinner. The effect of measuring at an increased time of mixing was studied through sample number 12, which was mixed for 12 minutes instead of 8 before taking velocity measurements. This sample demonstrates that the mixes get thinner as they are mixed (not uncommon in cement pastes), and underlines the importance of making measurements at similar time of mixing.

To determine how sensitive the tests were to changes in the seven day strength, the powers to stir the mixes at three defined velocities were extracted from the power/velocity plots and plotted against seven day strength of the corresponding sample. This process was done for the control samples only; comparing those samples containing different waste or water content would be inappropriate. The linear least-squares fit of the resulting scatter diagrams was determined, the correlation coefficient found, and the confidence level determined. The least-squares numerical values obtained is shown in Table III.

The data in Table III show that there is no significant correlation between the power and seven day strength for the first batch (OPC/4%) samples. This fact is explained by the existence of the first couple of samples which were created, which had lower strengths than the others but had similar consistency. The second batch of samples show a strong negative correlation. This result is initially disturbing, stating that the thinner samples were stronger. One possible explanation is that the degree of compaction was better in such samples. The third data group shows a strong positive correlation. This contradiction of the previous group can be explained by realizing that the slag cement is, after seven days, still relatively rapidly gaining strength compared to the OPC, which has a much faster initial reaction, but which is slower than the slag cement after seven days. The thicker slag cements may have some differentially lower w/c ratio which would magnify the strength changes since this cement is at seven days maturing faster than OPC. The thicker slag cements may be stronger than the thinner ones, therefore, while the opposite may be true for the OPC. A longer waiting period before testing would verify this hypothesis. It is, however, sufficient to say that there exists some definite relationship between the seven day compressive strength and the rheology of the mixture.

The rheology test thus proves to be a very good detector of mixture changes and the measured power to turn the shaft seems to be related to the product strength. Further analysis and experiments need to be done to clear up some interesting anomalies.

Maturity Analysis

The temperature-time development of the samples after pouring was monitored. It is important to note that the maximum temperature of the 15 cm uninsulated cube reached 90 centigrade for the OPC/4% waste samples, 77 centigrade for the OPC/12% waste samples, and 62 centigrade for the slag cement samples. The high temperatures observed would be magnified and may cause physical problems when upscaled to 200 liter drums. The reaching of saturation could also cause problems with the maturity function. In addition, some of the samples high temperature resulted in slight bowing of the cube sides, which may have affected compressive strength testing. The ambient temperature also seems to have a major effect on the results of the maturity.

From the given results, however, it appeared that faster initial temperature rise resulted in a better spread of values and a corresponding increased sensitivity of maturity to strength changes. Similar to that which has been done in the rheology analysis, the maturity of the cements was determined at four, five and six hours and was plotted as a function of seven day compressive strength. Since the maturity has been shown to fit an exponential function of strength, the natural logarithm of maturity has also been fitted to the corresponding strengths. The results of this fit, along with the values for the linear fit, have been tabulated in Table IV.

The results in Table IV show that the early maturity is very closely related to the seven day strength. In addition, the longer that the cement is allowed to cure determines the degree of certainty. This fact would have to be used in

TABLE III
Data for Least-Squares Fit of Power to Strength

Batch Description (cement/waste), speed (m/min)	Least-Squares Coefficients ($St = A^*pow + B$) A	B	Correlation Coefficient r	Confidence Level %
OPC/4 %				
16	0.516	224	0.068	--------
18	0.707	241	0.094	--------
20	-0.495	323	0.051	--------
OPC/12 %				
16	-0.858	42.9	0.787	96.3
18	-1.15	52.9	0.854	98.5
20	-1.59	67.0	0.848	98.4
HOC-A/4 %				
10	1.29	-34.4	0.716	88.9
12	1.61	-44.7	0.750	91.2
13	2.00	-59.6	0.701	84.6

TABLE IV
Least-Squares Fit of Maturity to Strength

Batch Descrip., Time	Least Squares Coefficient				Correlation Coefficient		Confidence Level (%)	
	Linear (str = A*mat + B)		Nat. Logarm. (str = C*ln(mat) + D)		Lin.	Log.	Lin.	Log.
	A	B	C	D				
OPC/4%								
4 hr	4.01	-6.83	28.1	-99.6	.790	.801	98.0	98.3
5 hr	11.6	-241	17.1	-51.2	.820	.834	98.7	99.0
6 hr	21.4	-523	15.7	-50.2	.853	.867	99.3	99.4
OPC/12%								
4 hr	6.66	22.9	18.6	-72.3	.786	.783	96.2	96.1
5 hr	7.88	84.1	32.2	-156	.932	.930	99.8	99.6
6 hr	15.0	21.1	26.6	-134	.977	.977	100	100
HOC-A/4%								
4 hr	2.71	17.1	42.2	-162	.881	.917	99.1	99.7
5 hr	3.11	47.7	45.0	-190	.831	.878	98.0	99.0
6 hr	3.26	98.2	41.6	-183	.712	.761	92.5	95.5

determining the amount of accuracy attainable in an on-line system, and defines what can be considered on-line.

The sensitivity shown by the maturity to the strength is acceptable, over the range of two N/mm^2 the maturity after 6 hours changes by about 40 °C-hr.

The samples which contained high water or waste were for the most part indistinguishable on the temperature-time and maturity-time plots (not shown). The maturity method is therefore much more useful in determining minor variations in the strength that a specific mix will exhibit than the rheology method discussed, but the rheology method seems to be able to detect great changes in water to cement ratio or mix consistency much better.

Ultrasonic Analysis

All attempts to relate the ultrasonic pulse velocity at four, five or six hours to the seven day strength failed. The ultrasonic machine which was available was extremely operator sensitive when applied to the slightly soft cement surface. Certain trends were apparent, such as the increase in pulse velocity, and thus strength, as the cement hardened.

The quality of the contact also seemed to affect the ultrasonic pulse velocity greatly. To alleviate the problem, petroleum jelly was applied to the probe and the surface of the waste form. The magnitude of the problem, though reduced, was still too great to yield intelligible results.

The addition of small glass plates to the surface allowed for readings to be taken much earlier. The glass to cement contact was still a problem in some cases, but sufficient data were obtained to make a plot of the development of the pulse velocity as the waste form cured.

The operator sensitivity, day to day reproducability, and probe contact problems proved to be overwhelming for the use of the ultrasonic test in early predictions of long term strength in this experiment. The well established reliability of nondestructive ultrasonic testing make it desirable, however, to further try to define an operable system using ultrasonics for process control. Certain findings in this experiment support further study in this area. The use of varying the pulse frequency was also not examined, and may be important.

Sensitivity To Water To Cement Ratio Changes

The single most important variable in the solidification of the liquid waste in terms of strength development is the water to cement ratio. The deviant samples created in batches two and three allowed for the testing of the sensitivity of the rheology and maturity tests to changes in water to cement ratio. Although there were not enough samples created to create a statistical basis, the general trends in the test results when subject to different water to cement ratios yield significant qualitative results.

Figure 4 shows the power to turn the shaft at 13 m/min and the maturity after six hours as a function of the water to cement ratio of the batch three (slag cement) samples. The average power and maturity were used for the control samples. A similar plot was made for the batch two samples. The limited amount of data (2 points) dictated that a plot not be made for the first batch of samples.The data on the graph (power and maturity) have been normalized to their highest value, so that both curves could be shown on the same plot.

The graph indicates that rheological analysis is much more efficient in detecting changes in water to cement ratio than maturity analysis. In fact, data indicates that the six hour maturity may not be at all correlated to the water to cement ratio. There is reason to believe that the rheology test is even more sensitive to w/c changes than the compression tester is. One sample with a two percent higher water to cement ratio than the control group turned out to have a similar (26.1 N/mm^2) strength to the control group average. The sample, however, was easily identified on the power/velocity plot. This

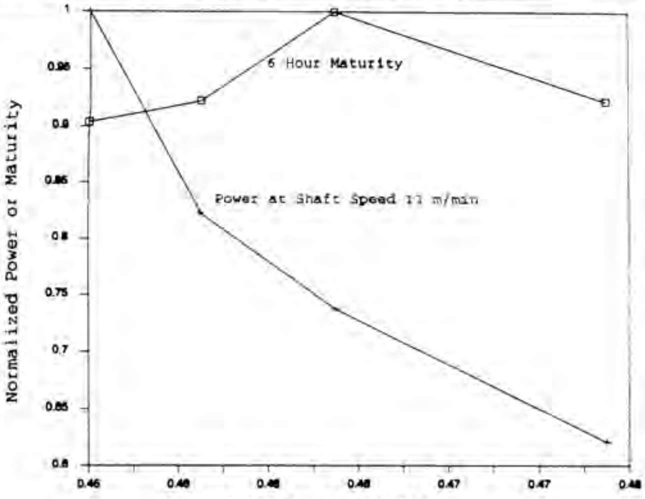

Fig. 4. Comparison of sensitivities of maturity and rheological analyses to water to cement ratio changes for OPC/BFS with normal waste load.

incident, while statistically meaningless, merits further investigation.

CONCLUSIONS

It is apparent from the obtained results that it is possible to predict the long term strength of the cement waste forms in the mixing or early curing stage, given a basis set of standards with which to compare. The quality of the mixes produced were acceptable, and in all cases appeared homogeneous. Some important parameters which affect the final product quality and/or measured quantities have been identified and include cement addition rate, mixture time, mixer (motor) type and paddle design, ambient temperature, and procedure (adding cement to waste or waste to cement).

Consistent operation was best monitored through plots of consumed power versus shaft speed. This technique was especially good at detecting water to cement ratio changes, to a resolution as low as two percent. Less control was attainable when slag cement was employed, which has been attributed to the higher blaine of that cement.

The relationship between power to turn at a given speed and seven day strength introduces some puzzling phenomena. Strong negative and strong positive correlations were observed for different mixes. The cause of this variation must be identified, and suggestions have been given.

The development of high temperatures in the waste form could be a problem in causing thermal stresses, evaporation, and fouling of maturity results upon scaling up to the production of 200 liter waste packages. In terms of low temperature development, the slag cement seems to be the best option tested.

The early maturity is an excellent indicator of the strength that a given sample will attain. Acceptable resolution is achievable after as little as four hours, but correlation and resolution tend to increase as time goes on. Linear and logarithmic analysis yield similar results over the small changes that exist, but the logarithmic correlation is slightly better on the average. The early maturity is not as useful in detecting small changes in water to cement ratio, and it was shown that the early maturity may not be a function of the water content at all. The attaining of a certain strength prediction, given a different water to cement ratio, is possible if maturity analysis is employed.

No intelligible data was able to be obtained that would relate early ultrasonic velocity to the long term strength. However, through refinement of procedure the use of ultrasonics was determined to show promise in detecting the time of setting of the waste form.

The final conclusion is that a combined testing procedure, employing both rheology and maturity analysis, is a possible method for insuring final product consistency and strength. Employment of these two tests, while economical, would create substantial knowledge concerning the predictable physical behavior of the waste forms.

REFERENCES

1. TATTERSALL, G. H. Workability and Quality Control of Concrete. (London, Chapman & Hall, 1991).
2. PRICE, M.S.T., Ed. "The Investigation of Non-Destructive Techniques for the Examination and Quality Assurance of Cemented Radioactive Waste". Winfrith project reference R 5649, 1985.
3. Betoniek. "Gewogen Rijphied". Betoniek 6/20(Nov/Dec 1984), pp 1-9.
4. KEMA. (Cornelissen, H.A.W. and Volgelsang, H.W.J.). "Process Description of Waste Treatment in the Netherlands". Report number 12376-CBP 91-678, 1991.
5. KEMA. (Cornellisen, H.A.W.). Annual Report 1. "Process Description and Inventories of Chemical and Radiological Characterizations". Report number 12376-CBP 92-21, 1992.
6. PALMER, J. D. and SMITH, D.L.G. "The Incorporation of Low and Medium Level Radioactive Wastes (Solids and Liquids) in Cement". CEC Report number EUR 10561, 1986.