# UTILIZATION OF USED CRACKER CATALYST AND LIME AS HYDRAULIC BINDERS FOR MORTARS

Harald Justnes,
Dr. Ing., Senior Research Engineer,
SINTEF Structures and Concrete,
N-7034 Trondheim, NORWAY,
Tel: +47-73 59 69 22, Fax: +47-73 59 71 36,
E-mail: harald.justnes@civil.sintef.no

**Abstract**
Used cracker catalyst waste consisting of zeolite on an alumino-silicate carrier have been demonstrated to form a hydraulic binder together with lime. When an alkaline accelerator is used, mortars based on such a binder achieve enough strength to utilize the product as for instance decorative bricks or panels. Compressive strengths of 6, 13 and 21 MPa after 1, 3 and 7 days curing may be achieved for press-moulded mortars using 3.9 % alkali carbonate accelerator of the binder weight.

Key words: Silicate, aluminate, lime, pozzolanic reaction, accelerators

## 1 INTRODUCTION

The reason for STATOIL to initiate the present study in 1988 /1/, was that the catalytic cracking part of the Mongstad refinery would produce about 6 metric tonnes of used RCC-catalyst each day, and restrictions on deposition of this waste. Due to its potential pozzolanic property and off-white colour, the utilization of the used catalyst as binder in for instance decorative stone (i.e. mortar) should be studied. Such a product could be an alternative to decorative stones made of autoclaved ground silica/lime, in particular since the production could be carried out at ambient temperature and moist curing. Today, the used RCC-catalyst is utilized as a part of the raw-material in a cement kiln producing white Portland cement.

The RCC-catalyst consists of 10-30% zeolite (i.e. an aluminosilicate) carried by a complex matrix based on kaolin (i.e. aluminosilicate), $SiO_2$, $Al_2O_3$ (both active and inactive) etc. Since silica is an acidic oxide and alumina is amphoteric (i.e. can react in both an acidic and basic manner), the RCC-catalyst is a candidate for the general principle of reacting an acidic/amphoteric oxide with a strongly basic oxide like lime CaO catalyzed by alkali hydroxides in water. This general principle was demonstrated by Justnes /2/ for the reaction between silica fume and lime with simulated pore water (KOH/NaOH = 2, and pH = 13), where also the strength of mortars based on such binders was tested. Since alkali hydroxide solutions are considered hazardous liquids, Justnes /3/ showed recently that it was possible to utilize solutions of salts with pH<12, which would form hydroxides *in situ* in reaction with lime, to accelerate the hydraulic binder formation from silica fume and slaked lime. The same type of indirect accelerators was used in the present study.

Recently, the pozzolanic activity of thermally activated metakaolin /4/ (component in the RCC-catalyst) and the reaction between lime and clay /5/ (both natural and calcined) have been documented.

# 2 EXPERIMENTAL

## 2.1 Components

The RCC-catalyst (Z) was obtained from STATOIL Mongstad and had a content of about 47 % $SiO_2$ and 44 % $Al_2O_3$. The used catalyst is separated from the continuous process by a cyclone and a filter. The particle size distribution revealed 50 % particles <3µm and 90 % < 10 µm. The slaked lime, $Ca(OH)_2$ (CH), and burnt lime, CaO (C), were industrial grades being > 96 % pure.

The accelerators 1 and 2 consisted of a 3:1 mix of potassium carbonate, $K_2CO_3$, and sodium carbonate, $Na_2CO_3$, and a 3:1 mix of potassium sulphate, $K_2SO_4$, and sodium sulphate, $Na_2SO_4$, respectively. All these salts were of "purum" quality (>98%).

The sand was dry DIN 1164 Normensand from Beckum, Germany, supplied in bags of 1350±5 g.

## 2.2 Methods

### 2.2.1 Mixing and curing procedure

In all mixes, two bags of sand was used for 1000 g RCC-catalyst (Z) + lime (C). The lime content is calculated as burnt lime, CaO, even when slaked lime, $Ca(OH)_2$, is used. Slaked lime is regarded as burnt lime and water ($CaO+H_2O$) and this water is incorporated in the total water/dry binder ratio.

The basis mix was 420 g RCC-catalyst (Z), 168 g burnt lime (C), 545 g slaked lime (CH) and 644 g water (H) with 50 g of a naphthalene based super-plasticizer. The use of burnt lime will lead to a certain temperature increase due to the exothermic reaction with water, which may help accelerate the early reaction rate. The amount of lime is calculated from the maximum consumption according to the content of alumina (A) and silica (S) in Z and the following chemical (pozzolanic) reactions:

$$3C + A + 6H = C_3AH_6 \qquad (1)$$

$$3C + 2S + 6H = C_3S_2H_6 \qquad (2)$$

Reactions (1) and (2) give a theoretical consumption of water to be chemical bound corresponding to a $H/(C+Z) = 0.37$ (compared with $w/c = 0.25$ for cement). In addition, there will be physical adsorbed water on the binder surface and water filled capillary pores. The basic mix corresponds to $H/(C+Z) = 0.80$. He et al /5/ confirmed that the reaction products of clay and lime accelerated by simulated cement pore water (i.e. pH = 13.2) were both calcium silicate hydrate and calcium aluminate hydrates.

The powders were pre-mixed before the liquid was added and the mix was blended for about 2 min in a Hobart mixer (model AE120) of 8 ℓ capacity. The mixes became rapidly earth moist and had to be strongly vibrated or tamped into six 40·40·160 mm steel molds. The 6 prisms were demoulded after 1 day and cured immersed in lime saturated water at 20°C.

### 2.2.2 Flexural and compressive strength measurements

The flexural strength was measured on two prisms and the compressive strength on the 4 resulting end pieces after 1, 3 and 7 days curing.

## 3 RESULTS AND DISCUSSION

### 3.1 General

In order to achieve the highest possible early strength for the binder (RCC-catalyst/lime/water), the following parameters were varied:

- Amount and type of accelerator.
- RCC-catalyst/lime ratio.
- water/binder ratio.

### 3.2 Effect of amount and type of accelerator

To types of accelerators were studied; 1) 3:1 $K_2CO_3$:$Na_2CO_3$ and 2) 3:1 $K_2SO_4$:$Na_2SO_4$, in three dosages; 1.3, 2.6 and 3.9 % of the dry binder content in the basic mix. There was a tendency of drier mix with increasing accelerator dosage, which also is reflected in faster setting and higher earlier strength. The masses, flexural strength and compressive strength of mortar prisms made from mixes with varying amount and type of accelerator are listed in Table 1. The compressive strength developments for the mixes with accelerator 1 and 2 are plotted in Figures 1 and 2, respectively. Compared with the silica /lime mortars tested earlier /3/, the compressive strengths (in particular 1 day) of RCC-catalyst/lime mortars were higher at similar dosage and type of accelerator and prism weight. This indicates a much more rapid pozzolanic reaction of the RCC-catalyst than for silica fume, which may be caused by the 10-30% zeolite part with high surface (i.e. in order to be an active catalyst).

### 3.3 Effect of lime content in the binder

Three mixes were made with less lime content than the theoretical maximum value used in the basic mix. The content of the alkali carbonate accelerator was kept constant to 3.9 % of binder weight. The ratio between burnt and slaked lime was kept constant as well, but when the total lime content is reduced the initial temperature will probably be reduced since the total amount of burnt lime is less. The mass, flexural strength and compressive strength of mortar prisms with Z/(C+Z) = 0.42 (basic), 0.50, 0.60 and 0.70 are listed in Table 2, while the compressive strength is depicted in Figure 3.

Table 1 Mass, m (g), flexural strength, $f_{fl}$ (MPa), and compressive strength, $f_c$ (MPa), of mortars based on catalyst waste as a function of time. Accelerator type and amount is varied.

| Accelerator | 1 | 1 | 1 | 2 | 2 | 2 |
|---|---|---|---|---|---|---|
| Amount | 1.3 % | 2.6 % | 3.9 % | 1.3 % | 2.6 % | 3.9 % |
| 1 day | | | | | | |
| m (g) | 541±3 | 530±7 | 534±5 | 536±9 | 542±5 | 529±3 |
| $f_{fl}$ (MPa) | 0.7±0.1 | 1.3±0.1 | 1.8±0.1 | 0.7±0.1 | 1.0±0.1 | 1.4±0.1 |
| $f_c$ (MPa) | 3.5±0.1 | 4.6±0.1 | 5.9±0.2 | 3.7±0.1 | 3.8±0.1 | 6.7±0.2 |
| 3 day | | | | | | |
| m (g) | 542±1 | 536±4 | 530±5 | 547±2 | 541±8 | 531±4 |
| $f_{fl}$ (MPa) | 1.5±0.1 | 2.4±0.2 | 2.9±0.1 | 1.4±0.1 | 2.0±0.1 | 2.7±0.2 |
| $f_c$ (MPa) | 7.2±0.2 | 9.6±0.5 | 12.5±0.6 | 6.3±0.2 | 7.8±0.6 | 12.3±0.1 |
| 7 day | | | | | | |
| m (g) | 535±4 | 536±1 | 533±2 | 538±1 | 541±7 | 536±3 |
| $f_{fl}$ (MPa) | 2.4±0.1 | 3.9±0.1 | 4.0±0.1 | 2.4±0.1 | 3.6±0.1 | 4.0±0.4 |
| $f_c$ (MPa) | 12.2±0.2 | 16.7±0.6 | 20.8±0.6 | 11.7±0.4 | 15.0±0.7 | 19.0±0.4 |

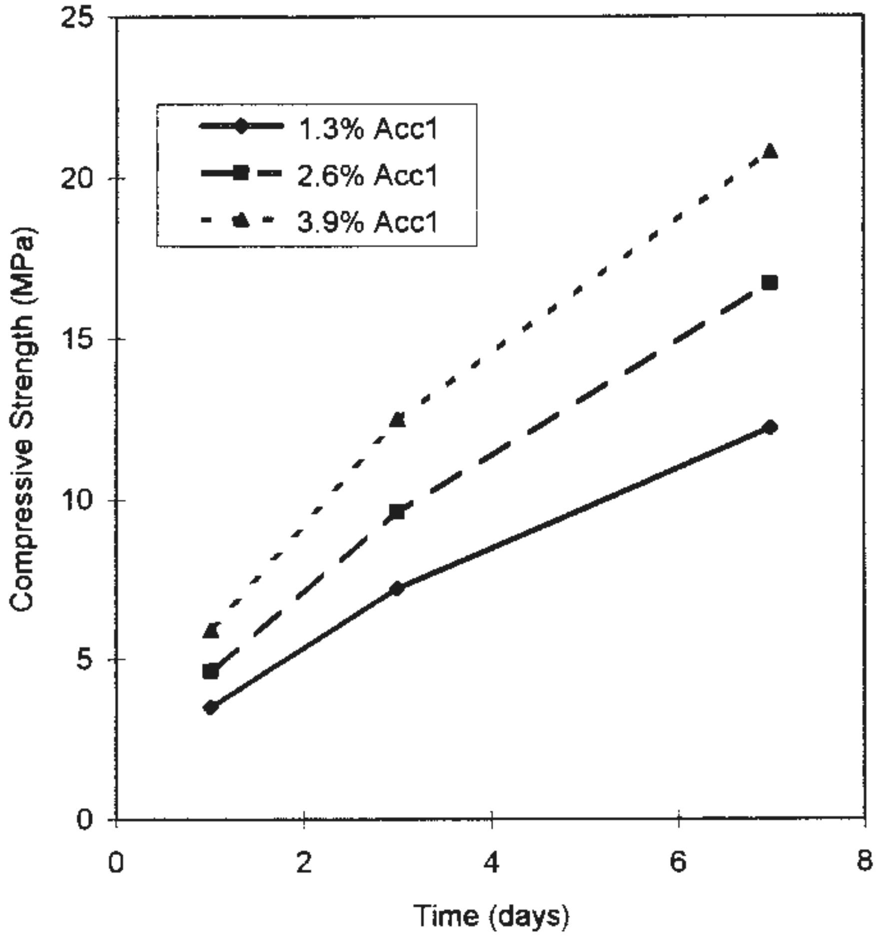


Figure 1 Development of compressive strength as a function of time for mortars based on RCC-catalyst/lime and different dosages of alkali carbonates.

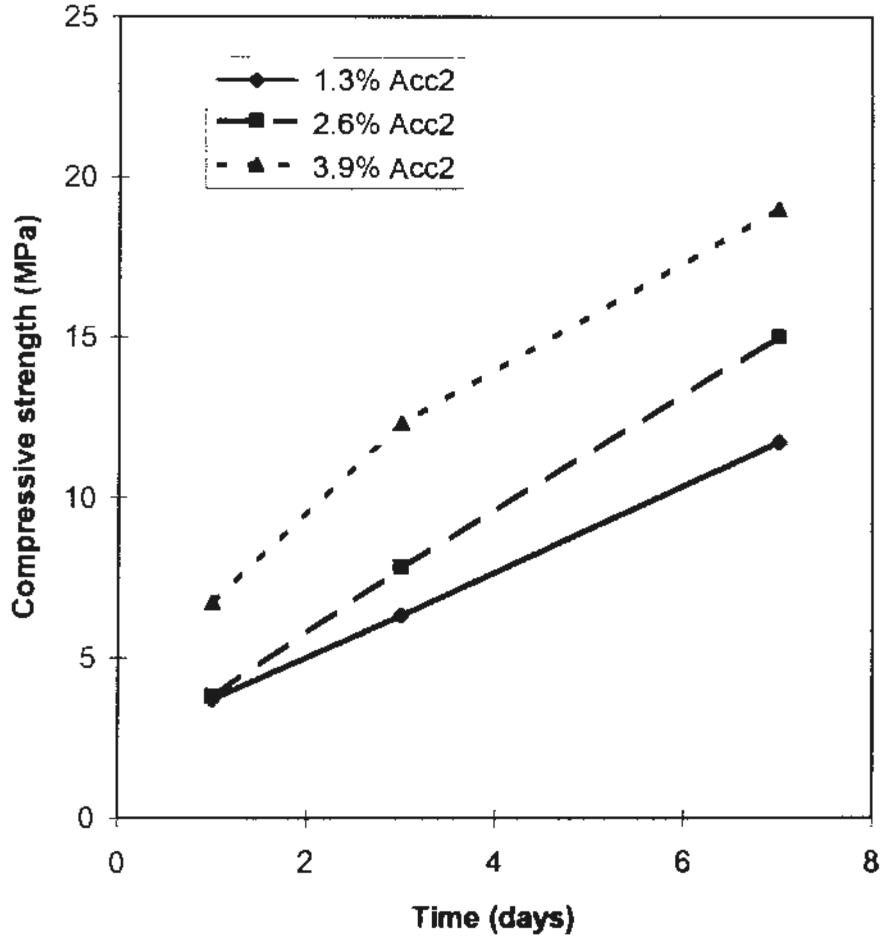


Figure 2 Development of compressive strength as a function of time for mortars based on RCC-catalyst/lime and different dosages of alkali sulphates

Table 2 The mass, m (g), flexural strength, $f_{fl}$ (MPa), and compressive strength, $f_c$ (MPa), for mortars as a function RCC-catalyst (Z) in the binder (C+Z) at different curing times.

| Z/(C+Z) | 0.42 | 0.50 | 0.60 | 0.70 |
|---|---|---|---|---|
| 1 day | | | | |
| m (g) | 534±5 | 468±14 | 502±4 | 482±1 |
| $f_{fl}$ (MPa) | 1.8±0.1 | 1.4±0.2 | 2.0±0.1 | 1.4±0.1 |
| $f_c$ (MPa) | 5.9±0.2 | 4.9±0.7 | 7.6±0.2 | 5.1±1.0 |
| 3 days | | | | |
| m (g) | 530±5 | 473±2 | 500±15 | 492±9 |
| $f_{fl}$ (MPa) | 2.9±0.1 | 1.8±0.1 | 2.5±0.1 | 2.1±0.1 |
| $f_c$ (MPa) | 12.5±0.6 | 7.1±0.7 | 12.3±0.4 | 10.0±1.6 |
| 7 day | | | | |
| m (g) | 533±2 | 443±32 | 500±14 | 466±21 |
| $f_{fl}$ (MPa) | 4.0±0.1 | 1.9±0.4 | 3.1±0.1 | 2.3±0.3 |
| $f_c$ (MPa) | 20.8±0.6 | 7.6±2.7 | 15.2±2.6 | 8.2±2.3 |

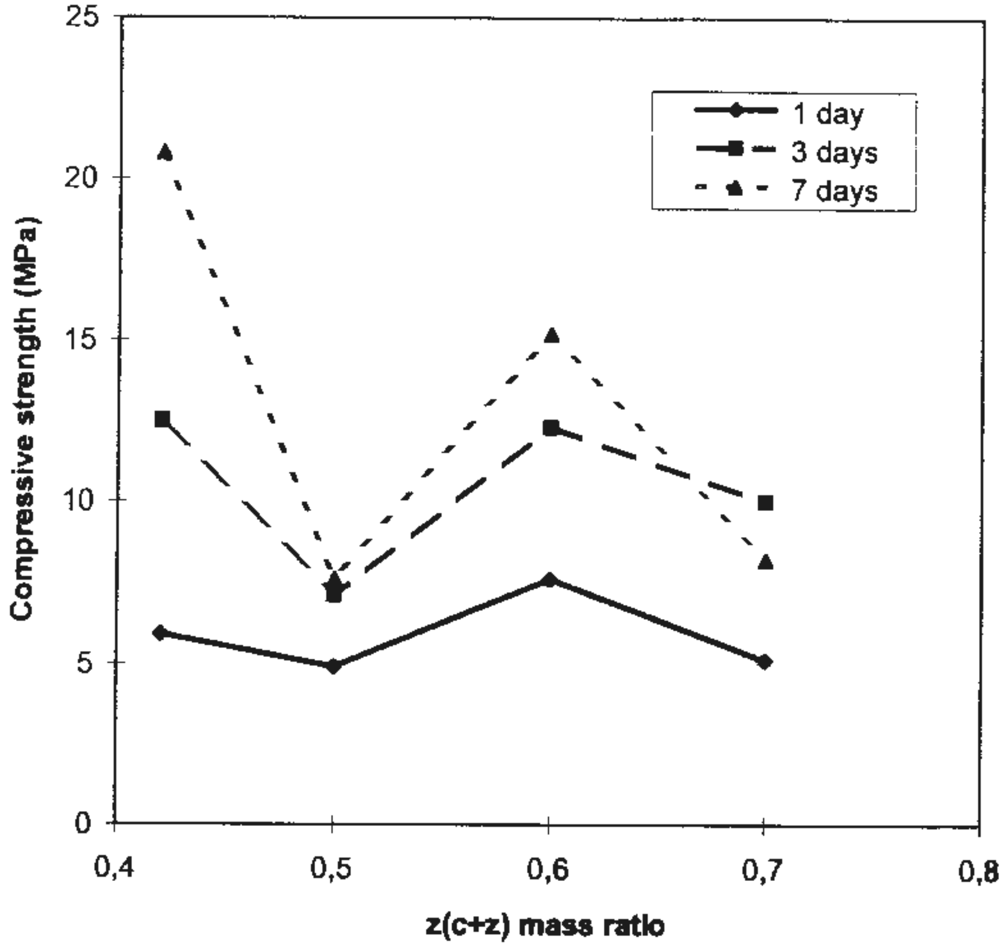


Figure 3 The compressive strength at 1, 3 and 7 days for mortars based on RCC-catalyst (Z) and lime (C) as a function of the Z/(C+Z) ratio

Apart from the mix with Z/(C+Z) = 0.50, which apparently was poorly compacted according to the prism weights in Table 2, there is a tendency of decreasing strength with decreasing lime content. The decreasing strength with decreasing lime content in the binder, could be explained by that the lime is nearly consumed at 7 days hardening. A mix with a higher lime content should have been investigated as well, in case other, more lime consuming, reactions occur than those sketched in Equations (1) and (2).

The large standard deviations for some of the strengths in Table 2 is probably due to poor casting and incomplete compaction by the tamping procedure. If an artificial stone was to be produced from the used RCC-catalyst, the automatic pressing or extrusion process would probably have lead to a more even and better compaction.

### 3.4 The effect of water-to-binder ratio

A mix with 100 g additional water compared with the basic mix was made as well. This mix was much more plastic than the basic mix and was thus probably better compacted in the molds. The mass, flexural strength and compressive strength of mortar prisms as a function of water-to-binder ratio are given in Table 3, while the compressive strength differences are shown in Figure 4.

Table 3 The mass, m (g), flexural strength , $f_{fl}$ (MPa), and compressive strength , $f_c$ (MPa) of mortar prisms based on RCC-catalyst and lime as a function of water-to-binder (W/B) ratio.

| water-to-binder ratio | 0.80 | 0.90 |
|---|---|---|
| <u>1 day</u> | | |
| m (g) | 534±5 | 515±4 |
| $f_{fl}$ (MPa) | 1.8±0.1 | 1.4±0.1 |
| $f_c$ (MPa) | 5.9±0.2 | 6.0±0.2 |
| <u>3 days</u> | | |
| m (g) | 530±5 | 524±5 |
| $f_{fl}$ (MPa) | 2.9±0.1 | 2.8±0.1 |
| $f_c$ (MPa) | 12.5±0.6 | 13.2±0.6 |
| <u>7 days</u> | | |
| m (g) | 533±2 | 524±5 |
| $f_{fl}$ (MPa) | 4.0±0.1 | 3.2±0.1 |
| $f_c$ (MPa) | 20.8±0.6 | 18.4±1.3 |

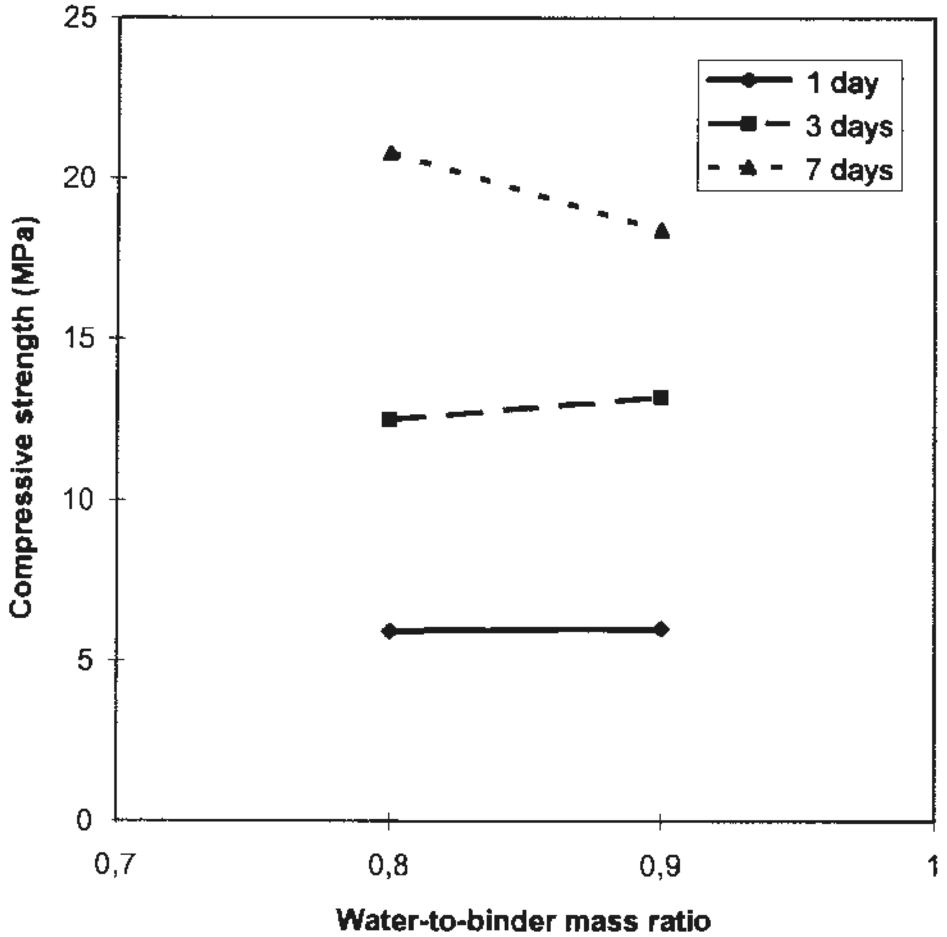


Figure 4 The compressive strength at 1, 3 and 7 days for mortars based on RCC-catalyst and lime as a function of water-to-binder ratio

According to conventional concrete technology, the strength should decrease with increasing water content due to increasing porosity in the binder. However, in this case the effect is partly counteracted by better compaction an more available water as solvent for the chemical reactions that are taking place. Only after 7 days, there is a significant reduction in compressive strength for the mix with most water.

## 4 CONCLUSIONS

It is possible to utilize used cracker catalyst as a hydraulic binder when it is combined with lime together with an accelerator creating high pH in situ.

Mortars and concrete based on such a binder could be produced by press-casting or extrusion.

The off-white colour of the binder makes the product suitable for decorative purposes (e.g. bricks or panels). However, before outdoor use can be recommended, the durability of the binder must be documented.

## 5 REFERENCES

/1/ Justnes, H. : "Utnyttelse av RCC katalysatoravfall som bindemiddel i kunststein - En forstudie", SINTEF Report STF65 F88014, 1988-04-06, 15 pp (In Norwegian).

/2/ Justnes, H.; "Hydraulic binders based on condensed silica fume and slaked lime", The 9th International Congress on the Chemistry of Cement, New Dehli, India, 23-28 November, 1992, Vol. III, pp. 284-290.

/3/ Justnes, H.: "Accelerated hardening of Mortars with Binders of Silica Fume/Lime", Nordic Concrete Research, Publication No. 17, 2/1995, pp. 30-41.

/4/ Zhang, M.H. and Malhotra, V.M.: "Characteristics of a Thermally Activated Alumina-Silicate pozzolanic Material and its Use in Concrete", Cement and Concrete Research, Vol. 25, No. 8, 1995, pp. 1713-1725.

/5/ He, C., Osbæck, B. and Makovicky, E.: "Pozzolanic Reactions of Six Principal Clay Minerals: Activation, Reaction Assessments and Technology Effects", Cement and Concrete Research, Vol. 25, No. 8, 1995, pp. 1691-1702.