SINTEF REPORT

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"Alternative pozzolans" as supplementary cementitious materials in concrete

State of the art

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ABSTRACT

This state-of-the-art report is a review of available literature on the pozzolanic materials calcined clays, light weight aggregate fines, rice husk ash, nano silica and ground glass as alternatives to the more common fly ash, slag, metakaoline and silica fume.

Calcined clay seems to have the greatest overall potential as alternative pozzolanic material for concrete due to its availability in large quanta and the relatively cheap price. However, the mineralogy of clays varies a lot, which may influence the reactivity. The optimum calcination temperature seems to be in the range 700-800°C, even though it may approach 1,000°C in some cases. The benefit of replacing cement in concrete is not on strength improvement, but more on durability enhancement. Calcined clay seems to be equally beneficial as light weight aggregate fines originating from similar clay but burnt at 1,150°C and ground to 5-10 µm.

Processed rise husk ash may be of interest for international active businesses since the availability seems to be concentrated far from Norway. However, the material is highly pozzolanic and improves both strength and durability of concrete when replacing cement.

Nano silica improves concrete properties like strength and permeability in relatively small dosages (0.5-3 % of cement). However, the high price means that cost/benefit should be evaluated as well as if it is possible to achieve similar properties by cheaper means. Ground recycled glass is too slowly reacting to be of interest as alternative pozzolan, although it may improve the rheology of concrete.

KEYWORDS	ENGLISH	NORWEGIAN
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SELECTED BY AUTHOR	Cement	Sement
	Pozzolans	Pozzolaner
	Calcined clay	Kalsinert leire

Foreword

COIN - Concrete Innovation Centre - is one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfill this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students every year and a number of international guest researchers, work on presently 5 projects:

- Advanced cementing materials and admixtures
- Improved construction techniques
- Innovative construction concepts
- Operational service life design
- Energy efficiency and comfort of concrete structures

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %). The present industrial partners are:

Aker Kværner Engineering and Technology, Borregaard LignoTech, maxitGroup, Norcem A.S, Norwegian Public Roads Administration, Rescon Mapei AS, Spenncon AS, Unicon AS and Veidekke ASA.

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1 INTRODUCTION

State-of-the-art report (STAR) on alternative pozzolans is a review of the use of "unusual" supplementary cementitious materials in concrete. Materials that are included in this report are micro-LWA, calcined clay, rice husk ash, nano-silica and glass. Common ones like silica fume, fly ash, slag and metakaoline are only mention as comparison.

Environmental concerns both in terms of damages caused by the extraction of raw material and CO_2 emissions during cement manufacture have brought about pressures to reduce cement consumption by use of supplementary materials. In addressing environmental problems and economic advantages, mixtures of Portland cement (PC) and pozzolans are very commonly used in concrete production [Sabir et al., 2001].

Cement production is a highly energy-intensive process involving significant environmental damage with respect to CO_2 production and raw material acquisition. STAR 1 in 11f is looking into solutions to this problem.

2 POZZOLANS IN GENERAL

2.1 Definitions, terms and classification of natural pozzolans

The definition of natural pozzolans according to ASTM Standard C618 is *siliceous or siliceous and aluminous materials, witch in themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.*

Within the building industry, the term "pozzolan" covers all the materials which react with lime and water giving calcium silicate and aluminate hydrates. All pozzolans have to be rich in reactive silica or alumina plus silica [Bensted and Barnes, 2002].

According to ASTM standard C618 the requirements to chemical composition of natural pozzolan are approximately 70 % in contents of silicon dioxide (SiO_2), aluminum oxide (Al_2O_3) and iron oxide (Fe_2O_3). The loss on ignition is required to be max 10 %, according to the same standard.

The acidic and amphoteric oxides (silica, alumina and ferric oxide) content vary widely from one pozzolan to another. Silica is a major component in natural and processed pozzolans.

Pozzolans are classified into natural materials and artificial. Artificial ones are mostly industrial by-products. Examples for both types are given in Table 1.

Table 1: Example of pozzolans [Müller, 2005]

	Pozzolan	**Active components**
Natural	Volcanic tuff	Aluminosilicate glasses, zeolites, clay minerals
	Rock from meteorite impact	Aluminiosilicate glasses, zeolites, clay minerals
	Diatomaceous earth	Fine grained silica rich skeletal remains of diatoms
	Bauxite	Aluminum hydroxides
Artificial	Calcined[a] clays or shales	Unstable dehydroxylation products of clay minerals
	Low-calcium fly ash	Glasses, calcined silicates and aluminates
	Condensed silica fume	Amorphous silicon dioxide
	Rice husk ash	Amorphous silicon dioxide

[a]According to Wikipedia, calcination (also referred to as calcining) is thermal treatment process applied to ores and other solid materials in order to bring about a thermal decomposition, phase transition, or removal of a volatile fraction. The calcination process normally takes place at temperatures below the melting point of the product materials. Calcination is to be distinguished from roasting, in which more complex gas-solid reactions take place between the furnace atmosphere and the solids.

2.2 Strength of pozzolan-lime paste and mortars

Strength of pozzolan-lime mixes increases as the amount of combined lime increases, but there is no general relationship between the two parameters. The strength development and the ultimate strength depend on pozzolan/lime ratio, water/binder ratio and the particle packing of the pozzolan material. The alkaline contaminants functioning as accelerators are also a factor. The rate of hardening is slow at start, but the long-term strength can reach about 20 MPa and this value high is enough for many applications. See Fig. 1. The maxima vary also in connection with other factors so that the best mixes must be established on a case-by-case basis [Bensted and Barnes, 2002].

The differences in pozzolan materials themselves are a factor that influences strength on the pozzolan-lime mortars. Justnes (1992) investigated silica –lime mixes and found compressive and flexural strength about 56 MPa and 8 MPa, respectively, after 28 days curing and slaked lime/silica fume ratio of 0.5.

While FA-lime on the other hand achieved compressive strength of approximately 35 MPa according to Malhotra and Dave (1999). Replacement of pozzolan for Portland cement causes decrease in early strength. This may be due to that pozzolan concrete having a higher w/c ratio caused by high specific surface of the pozzolan, or that the pozzolan has lower reactivity than the cement (e.g. fly ash). However, this may be compensated by finer grinding. Silica fume on the other hand, reacts faster than fly ash at early ages. The ultimate strength of pozzolan-containing cements can be higher than that of the parent Portland cement as shown in Fig. 2.

The time required to recover the initial strength loss caused by the replacement of pozzolan depends on the nature of pozzolans, including the content of the active phases and specific surface, the replacement level, the composition and the strength class of Portland cement.

Recommended replacement of Portland cement with pozzolan is 15-20 % for workability reasons (depending on fineness), and this is enough to comply with the pozzolanic test requirements.

Pozzolanic index: defined as the ratio of the compressive strength after 28 days curing of the test sample to the reference sample. According to ASTM C311 the test mixtures replace 20 % of the mass of the amount of cement used in the control mixture by the same mass of the sample.
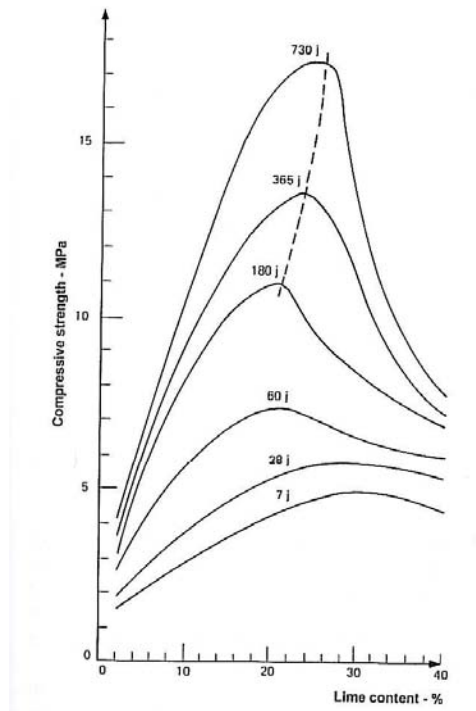

Fig. 1 Compressive strength of hydrated lime-pozzolan pastes versus lime content in the mix and w/b ratio of 0.56 [Bensted and Barnes, 2002]
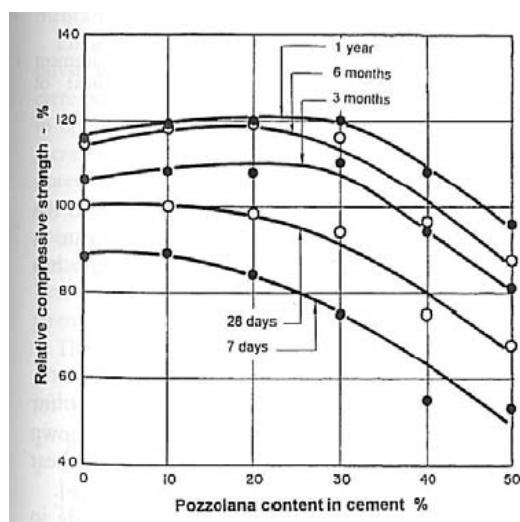

Fig. 2 Effect of pozzolan replacement for Portland cement on compressive strength of standard mortar. Values expressed as percentage of the 28 day strength of the control Portland cement [Bensted and Barnes, 2002].

2.3 Chemical composition of pozzolans

To determine the chemical characteristics of the clay materials and other pozzolan it's common to use X-ray fluorescense. These analyses are important since the total percentage of silica, alumina and iron of clays give a good indication of the quality of the produced pozzolanic material [Al-Rawas and Hago, 2006]. Most articles compare the chemical composition according to the ASTM standard 618 of natural pozzolans.

The total content of silica, alumina and iron oxide together with the burning temperature and duration of burning has an effect on the physical properties of the clay used as pozzolan in concrete.

2.4 Analytical methods for mineralogy of pozzolans

The mineralogical composition of clay materials can be characterized by X-ray diffraction (XRD) techniques. This is based on the fact that the crystalline fraction of clay materials interferers with the X-rays resulting in a characteristic diffraction pattern. By comparing with reference data, the qualitative compositions can be determined.

Scanning Electron Microscopic (SEM) investigations are based on the interactions of a focused electron beam in vacuum with a sample surface and rapidly moving electrons. These interactions lead to emission of secondary electrons (SE) and back scattered electrons (BSE) from the surface. SEM can give information on the topography, morphology, composition and crystallographic information of the samples.

Differential thermal analysis (DTA) can be used to determine the amount of the pozzolanic reaction and hydration of blended cement pastes [Vedalakshmi et al. 2003, Moropoulou et al. 2004, Dahl et al. 2007, Justnes and Østnor 2001] by estimating $Ca(OH)_2$ content and calcium silicate hydrate (CSH) content. The DTA curve shows a sharp endotherm signal between 450 and 520ºC due to the decomposition of $Ca(OH)_2$ formed during the hydration. $Ca(OH)_2$ consumption that takes place in lime/pozzolan pastes could be a reliable factor for the evaluation of the pozzolan reactivity and the formation of the pozzolanic products. For some DTA instruments a MS (Mass Spectroscopy) instrument can be connected, and the gases that are produced during for instance the decomposition can be determined.

Thermal analysis is also widely used to determinate the optimum range of calcination temperatures that will produce the highest pozzolanic activity for clays, since temperature for mass loss will be seen on the gravimetry curves (DTG), and eventual melting points can be seen on the energy curve exchange (DTA). See Fig. 3 [Cook, 1985].
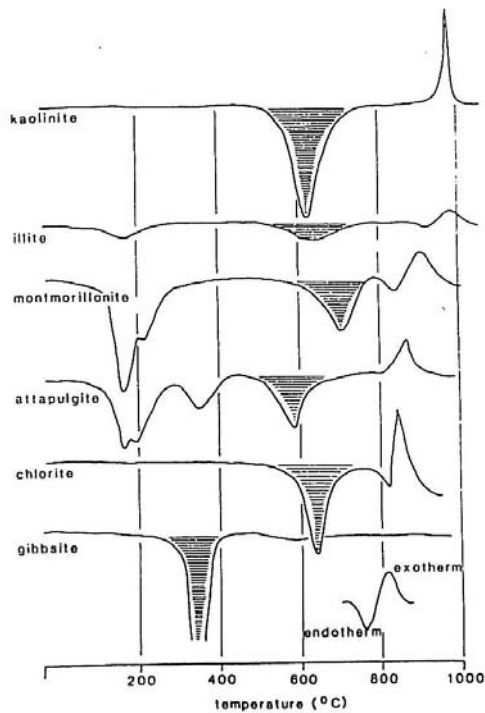
Fig. 3 Differential thermal analysis curves for the most common clay minerals [Cook, 1985]

3 LITERATURE REVIEW

3.1 Calcined clay

Clays are rarely found separately and are usually mixed with other clays and with microscopic crystals of carbonates, feldspars, micas and quarts. Clay minerals are divided into four major groups: kaolinite, montmorillonite/smectite, illite and chlorite groups.

The compositions of clay minerals depend on geographic area and the bedrock, and vary a lot all over the world.

According to Wikipedia is the plasticity index (PI) a measure of the plasticity of a soil. The plasticity index is the size of the range of water contents where the soil exhibits plastic properties. The liquid limit (LL) is the water content where a soil changes from plastic to liquid behavior.

Soils with high PI indicate the presence of high proportion of clay fraction, and soils with lower PI tend to be silt. Graphical representation of this is shown in Fig. 4.
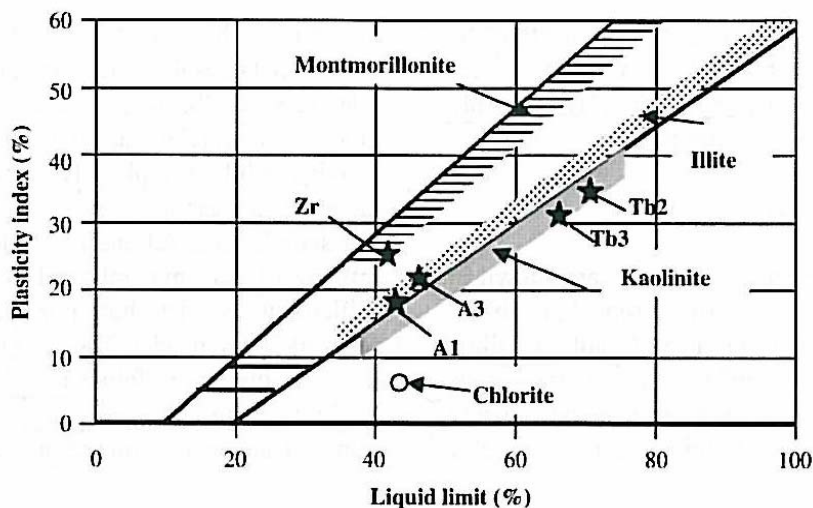
Fig. 4: Holtz and Kovacs diagram [Chakhouk, 2006]

Müller (2005) investigated the interaction between the non-calcined clay minerals (kaolinite, illite and montmorillonite) with lime from a soil stabilization perspective. However, in addition to simple ion-exchange between alkalis and calcium, he also observed a real pozzolanic reaction forming new hydration products after about a month. Diamond et al. (1963) also showed that non-calcinated clay minerals behaved as pozzolans in the order kaolinite > montmorillonite ~ mica ~illite > pyrophyllite, while talc did not react. The pozzolanic reaction of non-calcined clays are however to slow to be of interest for cement and concrete technology, and calcination seems necessary to make it a beneficial additive.

An advantage by using calcined clay as pozzolan in concrete compared with other pozzolanic materials is the access of the material all over the world and its low price, even though some energy has been spent on calcination.

A lot of researches have been performed over the years on clay mineral kaolin. Calcined kaolin gives metakaoline, a highly pozzolanic material not mention here. A review on metakaoline can be found in Bensted and Barnes (2005) and in a study by Soduza and Molin (2005), and is not a part of this report.

The optimal calcining temperature depends upon the nature of the clay mineral and the thermal energy required combining hydroxyl ions to oxide and water. Grinding can also be advantageous by braking up particle agglomerates and exposing additional surface for reaction.

Calcining natural pozzolans containing clay at 600- 800°C increases the performance, but it is ineffective on glassy or zeolitic materials. The thermal treatment destroys the crystal structure of the clay minerals witch is transformed to an amorphous and very reactive structure. Calcinations have therefore two positive effects [Bensted and Barnes, 2002]:
- It reduces the high water demand associated with the presence of clay minerals
- It increases the active phase content

The burning or calcining temperature of clays is crucial and affects the pozzolanic reactivity of the resulting product. The clay is in its most reactive state when the calcining temperature leads to loss of hydroxyls and results in a collapsed and disarranged clay structure. The calcining temperature producing the active state is usually in the range of 600-800°C [Sabir et al., 2001].

According to Forrester (1974) the optimum calcining temperature is not directly linked to the decomposition temperature of clay as indicated by DTA/TG. The strength of lime-calcined clay mixes drops significantly above a certain calcination temperature as shown in Fig. 5.
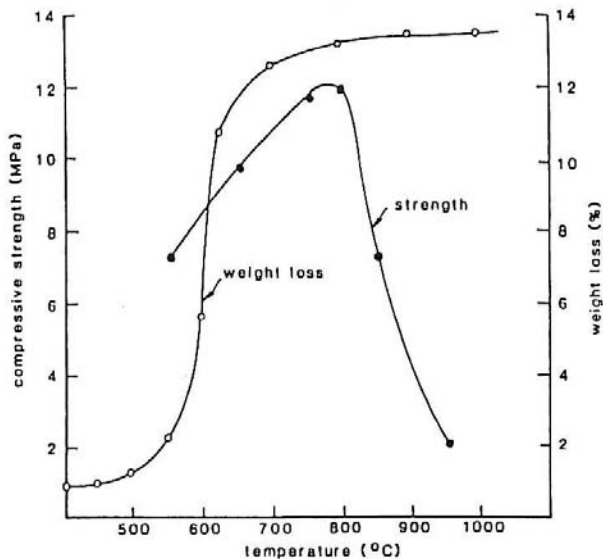
Fig. 5 Weight loss and pozzolanic reactivity as a function of temperature [Forrester, 1974]

Not only is the calcination temperature important, but also the length of time the clay experiences this temperature as illustrated by strength of lime-calcined clay mixtures by the same authors in Fig. 6.
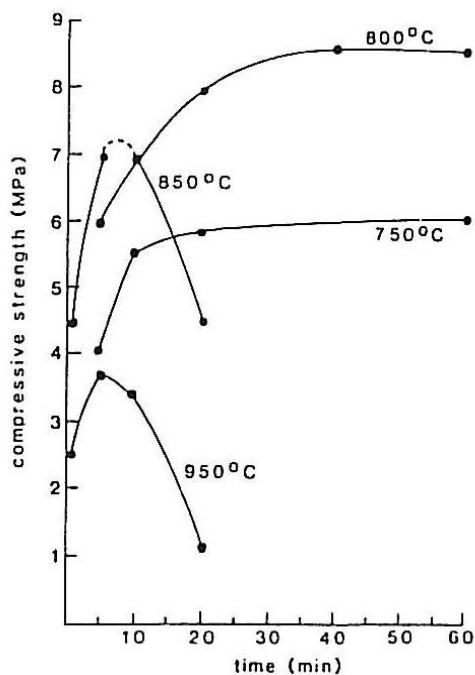

Fig. 6: Effect of temperature and time of activation on the strength of lime-pozzolan mortars cured at 50ºC for 7 days [Forrester, 1974]

Table 2: Effect of calcining on the structure change of clays [Shi, 2001], by using DTA.

Step	Temperature (°C)	Structure change
Step I	< 180	Loss of surface and adsorbed water
Step II	180-500	Dehydroxylation of the clay structure
Step III	600-800	Rupture of bonds and collapse of clay structure
Step IV	900-1000	Formation of new high temperature phases

In 1945 indicated Mielenz et al. that calcination will improve the quality of some pozzolans, reduce quality of other, and induce pozzolanic properties in some otherwise essentially non reactive-substances. After many year of research a number of clay pozzolan materials were tested for grindability and fineness, specific gravity, water requirement, time of set, reactivity with lime, compressive strength of mortar cubes and many chemical analyses. This report reviewed reactivity with lime, compressive strength and chemical analysis on clay types like montmorillonite, illite and mixed clays with vermiculite. The raw clay materials were calcined in a temperature range from 204°C to 1093 °C. The mix proportions on mortars by weight on all the calcined clay materials was water = 0.6, Portland cement = 0.65, calcined clay = 0.245 to 0.273 and sand = 2.42 to 2.56. For raw clay it was a water demand of 0.9 by weight, and the rest of the properties were the same as for the calcined clays.

Montmorillonite type clay [Mielenz et al, 1945] was changed greatly by calcination, and increased with calcination temperature. The water requirement for producing lime-pozzolan paste of normal consistency ranged form 32 to 165 %. The setting time of lime-pozzolan paste decreased markedly with calcination of the pozzolan, usually to a minimum after calcination at 538°C to 760°C. Calcination at higher temperatures increased the setting time. Compressive strength of Portland cement-pozzolan mortar increased with calcination, the maximum strength was obtained after calcination at 650, 760, 870 or 980°C, depended on the composition of the pozzolan. The highest compressive strength measured in average of all the samples was obtained by calcination at 760°C after 7 days curing.

Illite type clays [Mielenz et al, 1945] were affected significantly by calcination in the range from 425°C to 980°C. Water demand decreased moderately, especially after sintering of the clay by calcination at 980°C. Setting time of the lime-pozzolan was reduced to a minimum by calcination of the pozzolan at 760°C. Compressive strength of the lime-pozzolan mortar was improved slightly or moderately by calcination, and maximum strength was obtained after calcination at 960°C at 7 days of curing.

Mixed clay [Mielenz et al, 1945] was affected slightly by calcination to 980°C. Before calcination non of the materials in this group caused final set of lime-pozzolan paste at ages less than 1,000 hours, and some of them caused no final set of paste even after calcination at 535°C. The compressive strength of Portland cement-pozzolan mortar at age 90 days ranged from 50 to 91 % of that the control mortar, reaching a maximum after calcination at 980°C.

Pozzolanic reactions of six principal clay minerals were studied by He et al. (1995). Five so called standard clay minerals illite, Ca-montmorillonite, Na-montmorillonite, mixed layer mica/smectite and sepiolite were obtained from American Clay Minerals Society. Kaolinite was supplied by the Royal Porcelain. Chemical compositions of most clay conformed well to the pozzolan requirement in ASTM C 618 for the content of SiO_2, Al_2O_3 and Fe_2O_3. The sum of acidic and amphoteric oxides in the investigated clays was: Kaolin 82.0 %, illite 80.6 %, mixed layer mica/smectite 88.1 %, Na-montmorillonite 86.4 % and Ca-montmorillonite 86.7 %. It was not realistic to apply the compositional ASTM requirement on sepiolite because it's a magnesium

silicate with only traces of Al content. The loss on ignition could differ substantially from the values in ASTM because the values are depending on the atmospheric humidity. They meant that the threshold of the loss on ignition might be too tough for untreated clays that are characterized by high water absorption.

He et al. (1995) measured compressive strength of mortars on mini-RILEM prisms cured in water at 40°C for 28 days. The mortars had a ratio of cement, clays and sand of 70, 30 and 300 by weight, respectively. Kaolin compared with other clays and Ordinary Portland Cement (OPC) increases the compressive strength the most, up to 113 % of pure OPC when calcined at 550°C. And it remains in this range during further calcination up to 950°C. This indicates that it is economical to treat kaolin at 550°C to obtain a fairly good pozzolan. Illite on the other hand is a generally poor pozzolan even for the highest calcination temperature of 950°C. The maximum compressive strength of this mortar reaches only 70 % of that for 550°C kaolin. Ca-montmorillonite and Na-montmorillonite showed high compressive strength when calcined at 830°C. This is probably due to the content of amorphous SiO_2 achieved at lower calcination temperature, combined with particle size distribution and other factors. However, overheating to 930°C gave a substantial loss of mortar strength. The results are presented in Table 3.

Table 3: Compressive strengths (CS) in mortars containing untreated (U) and optimally calcined (O) clays and reference materials. The mortars after 28 days curing at 40 °C have a ratio of cement:clay:sand=70:30:300 in weight.

Sample	Optimum temp [ºC]	CS (MPa)		CS/OPC (%)		CS/550 ºC-kaolin	
		U	O	U	O	U	O
Kaolin	650	37.5	84.6	54	122		108
Illite	930	38.5	54.6	56	79		70
Ca-mont	830	53.6	86.7	77	125		111
Na-mont	830	29.8	78.1	43	113		100
Mixed layer	960	25.2	77.9	36	113		99
Sepiolite	830	14.2	58.3	20	84		74
Silica fume		78.4		113		100	
Slag		77		111		98	
Fly ash		61.1		88		78	
OPC		69.2		100		89	

The properties of laboratory and field burnt clay pozzolans from three sites in Northern Oman (Fanja, Al-Fulaij and Bahla) were studied by Al-Rawas and Hago (2006). The raw clays used in the study were classified as artificial pozzolans and burnt at 740°C for two hours. One purpose designed furnace to burn clays at the desired temperature was used for the laboratory burnt clay. The chemical compositions of the clay indicated the sum of SiO_2, Al_2O_3 and Fe_2O_3 of Fanja, Al-Fulaij and Bahla to be 80.9, 77.4 and 52. 8 %, respectively.

All tree clays were classified as clays of low activity [Al-Rawas and Hago, 2006]. The clay with the highest plasticity index was Al-Fulaij (23 %), and Fanja and Bahla have 20 % and 22 %, respectively. The clay content was Al-Fulaij (44 %), Fanja (20 %) and Bahla (22%). In 1998 indicated Al-Rawas et al. that high clay content gives higher compressive strength. Al-Fulaij clay was expected to produce a pozzolan with high compressive strength based on the clay content.

Fanja kiln-burnt clay obtained the highest compressive strength of 18.3 MPa after 28 days curing. Fanja laboratory-burnt clay obtained the highest compressive strength of 26.5 MPa after 90 days curing. Bahla kiln-burnt sample showed the lowest compressive strength, with a maximum of 4.8 MPa at 90 days. The strength results were as expected from the chemical composition, but not according to the clay content. Thus, the chemical composition and compressive strength results showed good agreement. The compressive strength result showed that all samples developed strength with time. All the mixes had proportions by mass: burnt clay = 1, lime = 0.33, sand = 0.67 and water = 0.5 (i.e. no cement).

Yogananda and Jagadish (1988) found also that some common burnt clay gave good pozzolanic activity. The mineralogy of these clays was not given (content of kaolinite unknown), but the chemical composition showed sum of SiO_2, Al_2O_3 and Fe_2O_3 > 70 % (requirement for good pozzolan according to ASTM 618) for the best ones.

Chakhouk et al.(2006) studied clays from five different locations in Tunisia calcined at 600, 700 and 800°C. The clays were named after sites of location: Mednine (A3), Zarmdine (Zr), Gabes (Gb) and Tabarka (Tb2 and Tb3). Geotechnical, chemical and physical properties of both untreated and calcined clay samples were determined. The pozzolanic activity of the calcined clay was evaluated by compressive strength performed on calcined clay-calcium hydroxide mini-cylinders. The chemical composition of the clay calcined at 800°C was determined by X-ray fluorescence. They compared the chemical composition with the ASTM C618 requirement and Indian requirement; the results are presented in Table 4.

Table 4: Chemical criteria for Pozzolanic activity of the calcined clays at 800°C [A. Chakchouck et al., 2006]

	ASTM requirement			Indian requirement	
	$SiO_2+Al_2O_3+Fe_2O_3>70\%$	$SO_3<4\%$	$LOI<10\%$	$CaO<10\%$	$SiO_2+Al_2O_3>50\%$
A1	88.54	0.30	1.64	3.12	82.24
A3	86.47	0.40	2.07	2.54	79.59
Gb	83.84	0.51	3.01	19.84	80.14
Tb2	96.74	0.57	1.54	0.34	95.48
Tb3	96.91	0.30	1.72	0.79	95.64
Zr	89.56	0.81	1.43	1.70	84.28

It was difficult to predict the pozzolanic capacity of samples A1, A3 and Zr based on X-ray diffraction (XRD) results. These samples were composed of a mixture of clay minerals and non-clay minerals. XRD patterns show that the clay minerals presence in the samples A3 and Zr was kaolinite, illite and montmorillonite. Such clay minerals can be capable of producing pozzolans according to theory. Sample A1 was kaolinite with illite presence, and the non-clay minerals in all the samples were mainly quartz and calcite. Sample Gb had a low plasticity index, a high $CaCO_3$ content (determined by calcimetry) and was essentially composed of quartz and calcite (according to XRD), so they concluded that the sample may not represent any pozzolanic activity.Table 5 shows the XRD results of the clay samples.

Table 5: XRD results

	Kaolinite	Illite	Montmorillonite	Quartz	Calcite	Others
A1	+	+		+	+	Muscovite
A3	+	+	+	+		Dolomite, hematite
Gb	+		+	++	+	
Tb2	++			+		Anatase
Tb3	++			+		Anatase
Zr	+	+	+	+		Albite

+ present.
++ abundant.

All the samples was ground to finer than 5 µm and heated from ambient to 600, 700 or 800°C for 5 hours using differential thermal analysis (DTA). From these data Chakhouk et al.(2006) chose to use range of calcination temperatures between 600 and 800°C, which ensure a complete dehydroxylation and avoids the structural reorganization. For kaolinite 600°C was sufficient to produce the dehydroxylation. DTA analyses indicated that in samples (A1, A2 and Zr) with mixtures of clay minerals, only kaolinite transformed into amorphous phase, while illite and montmorillonite was not activated by heat treatment less than 800°C. He et al. (1995) indicated that optimum calcination temperature for illite was 930°C.

Table 6: Compressive strength (MPa) of calcined clays (CC) – lime (CH) mixtures at different calcination temperature [Chakchouck et al., 2006]

Calcination temperature	CC/CH=1			CC/CH=3		
	600	700	800	600	700	800
A1	0.3	0.4	0.7	0.5	0.7	1.0
A3	1.4	1.5	1.4	3.0	2.5	3.9
Tb2	5.8	7.9	8.0	7.9	9.7	10.8
Tb3	9.4	9.7	8.8	9.5	11.9	9.8
Zr	1.2	1.7	0.7	1.1	2.1	2.5

The samples with the highest amount of kaolinite (see Table 5) obtained the highest compressive strength (Tb 2 and Tb3) as shown in Table 6.

A study on moler was performed by Johansen and Andersen (1989). Moler belongs to the group of natural pozzolans consisting mainly of a mixture of montmorillonite and siliceous diatom skeletons in the form of amorphous opal. The clay was burned at a temperature of 900 °C which dehydrates the clay and diatom components, and a mixture of amorphous silica and aluminum oxide was obtained. The chemical composition was determined by x-ray fluorescence to a total of 90.9 % SiO_2, Al_2O_3 and Fe_2O_3, and with loss on ignition of 2.2 %, and the pozzolanic activity index was determined to 78.8 %. The chemical content and loss on ignition are acceptable according to ASTM C 618 and ASTM C311 requirements, respectively

For investigating the behavior of concrete containing calcined clay Detwiler et al. (2001) used calcined clay either as an admixture or as a component of blended cement. Four concrete mixtures with water-cementitious materials ratio (w/cm) of 0.4 were studied. Type I cement with 20 % calcined clay admixture by substitution, 68 % type I cement + 17 % calcined clay admixture + 15 % class C fly ash, type I cement with 30 % calcined clay admixture by substitution and type I cement only (control mixture) were studied. With respect to resistance to chloride-ion intrusion,

the 20 % and 30 % calcined clay concretes showed about the same results, with apparent diffusion coefficients of about 1/3 of the control. All the three combinations containing calcined clay produced acceptable results on alkali-silica reactivity tests. The compressive strength was tested according to ASTM C39, and all specimens meet the required 28 days strength of 40 MPa. The results showed that use of calcined clay improved the properties of the concrete in all of the dosages tested. All of the mixture combinations were better than the control.

A recent study done by Fernandez et al (2007) on Cuban clay using X-ray diffraction identified the illite and montmorillonite type clay. The content of SiO_2, Al_2O_3 and Fe_2O_3 was 57.7 %, 18.7 % and 7. 1 %, respectively. Hydration and pozzolanic reactions were stopped at 1, 7, 14 and 28 days on pastes where 30 % of Ordinary Portland cements were replaced with calcined clay. Calcination at 800°C with rapid cooling of the clay gave the best pozzolanic clay based on microstructure analysis.

3.2 LWA fines

Mirza and Al-Noury (1988) worked on pozzolanicity of LWA fines according to the literature search, but look relevated that this was fines from excavation of natural light weight materials (e.g. pumic stone) rendering this as a natural pozzolan, which is not a part of this report.

Zhang (1993) studied the pozzolanic activity of three finely ground LWAs; Liapor 8, HS Leca and Lytag. They were ground to Blaine finenesses 459, 467 and 371 m^2/kg, respectively, and replaced a low alkali Portland cement by 16 % keeping w/(c+LWA) = 0.5. The change in calcium hydroxide content after 7 months sealed curing at 20°C was determined by DTA/TG. The sum of SiO_2, Al_2O_3 and Fe_2O_3 was 86.6, 85.7 and 89.6 % for Liapor 8, HS Leca and Lytag, respectively. However, after curing the content of calcium hydroxide in OPC and OPC replaced with 16 % Liapor 8, HS Leca, Lytag and silica fume (as reference) was 24.3, 21.9, 21.5, 21.5 and 5.8 g/g ignited cement, respectively, corresponding to only 11% reduction by the LWAs compared to 76% by SF. The low pozzolanic activity of the LWAs here compared to that of Dahl et al (2007) studying Leca fines of 5 µm could be the lower fineness of about 15 µm (since Blaine was about same as cement) and the low alkali level of the cement (about 0.6 % Na_2O_{eq}) that could catalyze the pozzolanic reaction. Alternatively, the high strength Leca could have a different composition or been fired at higher temperatures than ordinary Leca.

Dahl et al. (2007) studied finely ground lightweight aggregate (micro LWA by maxit) as pozzolan material. The chemical composition was in total of SiO_2, Al_2O_3 and Fe_2O_3 82.3 %. This material is clay burned at a temperature (1,150°C) leading to sintering and glass formation. They found that such cement replacement material increased the concrete resistance to chloride ingress, reduced alkali aggregate reactions and increased the sulfate resistance. It was also possible to make concrete with good resistance to freezing and thawing cycles when 15 % 5 µm Micro LWA replaced the cement content. By replacing 15 % of the cement content with micro LWA the compressive strength was more sensitive to temperature and time. The conclusion was that the compressive strength at 28 day curing was 10-15% lower at 5°C, about equal at 20°C and 15 % higher at 35°C compared with the reference mix.

3.3 Rice husk ash (RHA)

Formerly, the main use of rice husk (RH) was as fuel in rice paddy milling process. The use of this fuel generates a huge volume of ash. The rice husk ash (RHA) had then no useful application, and was usually dumped into water streams causing pollution and contamination of springs. Recently, modern power plants are fueled by RH (e.g. Thailand) making RHA more available industrially in lager quantities.

Because rice husk ash is available in many parts of the world, and in large quantities, makes it an interesting by-product for use as supplementary cementing materials in concrete. The presence of mineral admixtures in concrete is known to impact significant improvements in workability and durability. Rice husk ash is classified as an artificial pozzolan according to Table 1.

By burning the rice husks under a controlled temperature and atmosphere, a highly reactive rice husk ash is obtained. The amorphous states were obtained from the ash because of the suddenly cooling of the rice husk after burning. Some indicate that this ash consists of non-crystalline silica and produces similar effects in concrete as silica fume. However, unlike silica fume, the particles of rice husk ash possess a cellular structure, which is responsible for the high inner surface area of the material even when the particles are not very small in size [Coutinho, 2003]. Unlike other pozzolanic materials, the concrete incorporating the RHA shows excellent strength development at early-age even without steam-cure [Wada et al., 2000].

Rice husk consist of about 40 % cellulose, 30 % lignin group and 20 % silica, and hence the ash contains a large amount of silica [Chindaparasirt et al. 2007 and Coutinho 2003]. The chemical composition is important for pre-treatment to be given to rice husk for further processing, and it's found to vary from sample to sample. The differences in the type of paddy, crop year, climatic and geographical conditions, in addition to the sample preparation and method of analysis, could be the reason for this variation [Chandrasekhar et al., 2003].

When rice husk is burned at temperatures 550 - 700°C, rice husk ash with cellular microstructure is produced. Burned rice husk give 14-20 % ash by weight which contains approximately 90 % by weight silica and minor amounts of other elements.

Rice husk ash contains high silica content in the form of non-crystalline or amorphous silica. That makes rice husk ash suitable for use as a pozzolan to replace part of the Portland cement content. The reactivity of rice husk ash as pozzolanic material depends on the crystalline/amorphous ratio and varies with the source of rice husk ash. And the quality of ash prepared depends on various heating conditions like temperature, rate of heating and soaking time [Chandrasekhar et al., 2006]. Thus, the evaluation of the amount of amorphous silica becomes very important.

Rice husk ash is slightly blackish due to the presence of unburned carbon. Rapid heating of the rice husk does not allow the oxidation of carbon before the surface melting occurs, which result in a higher amount of black particles. Lower heating rate reduces the amount of black particles because the oxidation of carbon takes place before surface melting of silica. By treating the rice husk with diluted acid the carbon content reduced. Followed by etching it can be prepared pure white amorphous silica [Chandrasekhar et al., 2006].

The enhancement of resistance to chloride penetration is also one benefit from using rice husk ash as pozzolan. The improvement is mainly caused by the reduction of permeability/diffusivity, particularly to chloride ion transportation in the blended cement concrete.
[Sarawathy and Song, 2007]

In 2001 Coutinho replaced 10 %, 15 % and 20 % of the cement content with Portuguese rice husk ash. Strength at 80 days, capillary absorption and chloride resistance was carried out to evaluate the durability of concrete made with RHA. The rice husk was incinerated in an oven heated up to 650 °C, and maintained at that temperature for 8 hours, then cooled down to room temperature and the RHA was ground. The strength of the RHA mixes was compared with a control mix (not added RHA) and a mix with 10 % silica fume after 80 days of curing. Results in Table 7 shows that using RHA as partial cement replacements enables higher compressive strength than the control concrete (0 % RHA) and also higher than 10 % silica fume concrete.

Table 7: Compressive strength after 80 days curing.

Sample	Strength (MPa)			
	1	2	3	Average
Control (0 % RHA)	36.2	35.4	33.7	35.1 ± 1.3
10 % Silica fume	39.4	38.6	38.1	38.7 ± 0.7
10 % RHA	41.0	42.3	41.2	41.5 ± 0.7
15 % RHA	40.7	44.3	40.1	41.7 ± 2.3
20 % RHA	42.6	42.7	43.7	43.0 ± 0.6

A study on the sulfate attack resistance and compressive strength by adding RHA was performed in 2007 by Chindaparasirt et al. Rice husk were burnt at temperature 600°C and the ash was ground in a laboratory rod mill to reasonable fine particles. RHA contained high silica content (90 %) and low loss on ignition (3.2 %) that suggested RHA was burned relatively complete. RHA were used in replacement dosages of 20 % and 40 % of Ordinary Portland Cement (OPC).

Expansion of mortar prism immersed in 5 % sulfate solution and the change in the pH values of the solution were monitored for mixes with fly ash and RHA. It was found less calcium sulfate and much less ettringite formation in mortars blended with RHA. This was confirmed by using SEM.

For RHA mixes the initial compressive strength was low due to the high water-to-binder ratio for the mixes, because of high water demand. For replacements level of 20 % RHA, the strength at 28 days of curing in water was 54 MPa, although the W/B ratio was higher than for the OPC mix giving 51MPa.That indicated RHA was quite reactive and resulted in hydraulic binder. They concluded that RHA at a dosage of up to 40 % cement replacement was effective in providing sulfate resistance that together with reasonable compressive strength development for the concrete.

Rice husk from Vijayawanda, India were studied by Chandrasekhar et al. (2006). The rice husk were boiled in 0.1 N HCl for 1 hour and then washed thoroughly with distilled water. The rice husk not treated with acid as well as the acid treated was heated at different temperatures from 500-1000 °C. The effect of the heating rate was characterized with X-ray diffraction patterns. The study indicates optimal temperature of 700 °C and soaking time for 2 hours for the preparation of amorphous and reactive silica from rice husk.

Chandrasekhar et al. (2006) used standard wet chemicals methods supported with instrumental techniques to determine the chemical composition. The samples were treated with saturated $Ca(OH)_2$ solution which reacted with the silica, and unused Ca was estimated by complexometric titration. The SiO_2 content in acid treated and untreated RHA was 97.8 and 89.5 %, respectively. The loss on ignition (LOI) in acid treated and not treated ash was 1.85 % and 2.11 %, respectively. Despite of the presence of black carbon particles in the untreated ash, it is interesting to note that the LOI was almost the same in acid treated and untreated RHA. That could indicate that the black particles are acid insoluble carbon. The cause of this can be due to the fact that potassium in the rice husk causes surface melting at low temperature, so the carbons gets entrapped giving black color to the ash.

According to NS-EN 13263-1 for silica fume, the SiO_2 content requirement is > 85 %. The rice husk ash complied with the requirement of SiO_2 content for both samples. These correspond with the fact that rice husk ash from Vijayawanda in India is a pozzolanic material.

Highly reactive pozzolanic rice husk ash was studied as a supplementary cementing material in 2003 by H. Yamamichi et al. 100x200 mm concrete cylinders were moist cured at 20°C and 85 % relative humidity for 2 days, and then cured in water at 20°C determination of the compressive strength at 3, 7, 28 and 91 days. At both 3 and 28 days of curing the compressive strength incorporating rice husk ash was higher than for the reference mix. The concrete containing RHA percentage of 0, 10, 20 and 30 % at the age of 7 days showed compressive strength of 39.6, 53.0, 65.0 and 70.9 MPa, respectively. Thus, the compressive strength for concrete with RHA was approximately 34-80 % higher than for the control concrete with 0 % RHA. The strength of concrete with RHA increased with time for all dosages of RHA.

Wada et al. (2000) investigated also highly reactive rice husk ash. The effect of the RHA on strength and durability was reported in the paper. They found that the compressive strength of the mortar and concrete were significantly improved by the RHA addition, and higher than those are for the control mortar and concrete. Recently studies showing increased compressive strength are also reported by Ganesan et al. (2007), Giaccio et al. (2007), Chindaparasirt and Rukzon (2007) and Feng et al. in 2003 as well.

3.4 Nano-silica

Recently, nano technology has attracted considerable scientific interest due to the new potential uses of particles in nanometer (10^{-9} m) scale. The technology of nano-structured materials is developing at an astonishing speed, and will be applied extensively on many materials. Although cement is a common building material, its main hydrate C-S-H gel is a natural nano-structured material. The use of nano-silica (NS) as supplementary cementing material in concrete is not as well investigated and documented as silica fume (SF). It is common knowledge that SF has a high pozzolanic activity and normally considered as the best mineral addition used for concrete. Studies (Collepardi et al. 2004) show that production of concretes with nano-silica can save the amount of silica fume whose availability on the marked is decreasing.

The pozzolanic reaction between SF and CH during cement hydration starts generally after 3 days of hydration, but Justnes et al. (2002) found pozzolanic activity after one day. By using ultrafine particle size as NS the specific surface and the number of atoms in the surface will increase. The nano-scale size of particles can result in improved properties from conventional grain-size materials of the same chemical composition. The studies on nano-silica use silica fume as comparison, because SF has been studied for many years. Björnström et al. (2004) questioned whether the more rapid hydration of cement in the presence of nano-silica was due to its chemical reactivity upon dissolution (pozzolanic reactivity) or to the high surface activity.

Schwarz et al. (2007) meant that the setting and hardening phases of cement hydration was accelerated by the presence of nano-silica in mixtures. They also claimed that nano-silica modified pastes exhibit in a significant degree of matrix densification at early ages, and that it could be observed from their conductivity response as well as compressive strength results. However, compressive strength results in some studies (e.g. Qing et al. and Schwarz et al) show higher strength at earlier age compared with silica fume. This could mean that NS modifies formed CSH directly by incorporation rather than forming more CSH through pozzolanic reaction as with CH and SF.

Qing et al. (2007) compared the influence of nano-silica (NS) added in cement paste with silica fume (SF). Both NS and SF in the study were commercially available materials, supplied by Mingri Nano-material Ltd. and Zhunyi Ferralloy Ltd. in China, respectively. The content of SiO_2 was 99.9 % for NS and the chemical composition of SF was 92.1 % SiO_2, 2.04 % Al_2O_3 and 1.08 % Fe_2O_3. The XRD powder patterns of NS and SF showed a strong broad peak characteristic for amorphous SiO_2.

For all the cement pastes, a cement plus addition: water:superplasticizer ratio of 1:0.22:0.025 was used. Test specimens were produced by replacing the cement with 2, 3, and 5 % SF and 1, 2, 3 and 5 % NS by weight. The control mix was without NS and SF. It was found that the compressive strength of all the mixes with NS was higher than for the control mix, and especially at 3 days of curing. Furthermore, with increasing the NS content, the paste strength increased. Increasing the SF content lead to a lower strength than for the control mix at 1 and 3 days of curing, but at ages of 28 and 60 days increasing strengths with increasing SF content were higher than those of the control mix.

Byung-Wan et al. (2007) studied cement mortars with NS replacement of 3, 6, 9 and 12 % by weight of cement. To compare the compressive strength, cement mortars with 5, 10 and 15 % SF by weight of cement were produced. The SF used in the study was in a powder form, and the NS is particles with SiO_2 content of 95 % and 99.9 %, respectively. The compressive strength development for mortar mixtures containing NS was all higher than that of the control (SF) cement mortars with the same w/cm ratio of 0.35. That could indicate that the nano-particles are more effective in pozzolanic reaction than SF. A higher content of NS must be accompanied by adjustments of the water and high-range water-reducing admixture dosage to ensure that specimens do not suffer from excessive self desiccation and cracking, as well as maintaining castability. It was not observed in the study that the use of high quantity of NS reduces the compressive strength of composites instead of improving it. However, they suggested that the optimum content of NS should be 6 % at a w/cm ratio of 0.23.

Li et al. (2004) reported the mechanical properties and the SEM observation of mortars mixed with nano-silica. They replaced 3, 5 and 10 % of the cement with nano-silica with 99.9 % SiO_2 at a w/b ratio of 0.5 for all the mixes. The compressive strength for all the specimens at 7 and 28 days of curing were higher than for the plain cement mortar with the same w/b ratio. 10 % replacement of cement with nano-silica obtained the highest compressive strength of 21.3 and 36.4 MPa at 7 and 28 days, respectively. The nano-silica was effective in improving the strength, with increasing amount cement replaced. The SEM observations also revealed that the nano-silica was not only acting as filler, but also as an activator to promote hydration. If the nano-particles were uniformly dispersed it could improve the microstructure of the cement paste as well.

Shih et al. (2006) studied a liquid form of nano-silica particle (40.6 % SiO_2 of slurry weight) in five different dosages (0, 0.2, 0.4, 0.6 and 0.8 % by weight) added to the Portland cement paste. The compressive strength increased with amount of nano-silica until it reached an optimal amount of 0.6 %, and then dropped to some lower value at 0.8 % addition. Addition of 0.6 % obtained the highest compressive strength at all ages with the highest value of 65.6 MPa after 56 days of curing. The much lower dosages of NS suspensions required than for the NS powder used in other studies indicates a much better distribution in the matrix.

3.5 Glass

Recycling of waste glass poses a major environmental problem. Moreover, waste glass is potentially a very useful material and appropriate economical applications need to be found for it. Glass is a unique inert material that could be recycled many times without changing its chemical properties. Unfortunately, a lot of glass become unsuitable for use or sent to landfill.

A major concern regarding the use of waste glass in the alkaline environment of concrete is related to susceptibility to alkali-aggregate-reaction (AAR). This property has been used as advantage by grinding it into a fine glass powder for incorporation into concrete as a pozzolanic material. Glass could fit in to the features for pozzolanic material such as, the high content of silica, amorphous material and large surface area. Glass could be ground to a size fine enough to passify the alkali-silica reaction and to activate the pozzolanic behaviour [Shao et al. 2000].

Chen et.al has shown in laboratory that the chemical composition of the glass does not vary a lot, with the exception of alkali that varies from 0-22 %. Utilizations of waste glass used as aggregate in concrete [Shayan and Xu, 2004 and Dahl, 2000] have also been evaluated.

Some studies have been performed regarding the use of glass as a pozzolanic material. In 2005 Shi et al. researched glass powders due to their particle size and specific surface area. It was found that the finer glass powder, the higher was the pozzolanic reactivity. Results form testing indicated that 20 % replacement of cement with ground glass powder also reduced the AAR-induced expansion, although it is not as effective as coal fly ash.

The most recently studies on plain and coarse glass powder was in 2007 by Schwartz et al. They found that the glass powder replaced with 10, 20 and 30 % cement gave a lower compressive strength than the control with no additive. This may be due to reduction in the cement content and increased effective w/c, which increased the porosity.

Klingstedt et al. (1993) investigated glass filler as additive to concrete. They focused on rheology but also acknowledged a slow pozzolanic activity.

4 FUTURE RESEARCH

Among the alternative pozzolans, calcined clay is perhaps the most interesting to pursuit due to its availability and relatively cheap price coupled by the relatively low energy demand for calcination. However, clays differ a lot in composition and efforts should bee made in finding good clay (screening) before detailed studies are continued for the most promising ones.

Rice husk is also an interesting alternative pozzolan to look into, although the availability is far from Norway. It may also need some further processing before it can be used in concrete.

Nano silica seems to be an expensive way of obtaining properties that may be achieved by cheaper means and is thus not recommended to look further into. However, an eye should be kept on on-going international research.

The pozzolanic activity of ground glass seems too slow to be of interest for further studies.

5 CONCLUSION

The available literature on the pozzolanic materials calcined clays, light weight aggregate fines, rice husk ash, nano silica and ground glass as alternatives to the more common ones, like fly ash, slag, metakaoline and silica fume, has been reviewed.

From this perspective, calcined clay seems the most interesting one to focus on in further research both due to the overall availability and low price. The pozzolanic activity depends on the distribution of minerals in the clay and efforts should be taken in finding a few good sources. The calcination temperature and time is also of importance and temperatures in the range 700-800°C seems in many cases sufficient. Calcined clay seems to be equally interesting from a durability point of view rather than just strength in concrete applications.

Light weight aggregate (LWA) fines consist of clay being burnt to a temperature where sintering and formation of glassy aluminosilicate have occurred. When LWA have been ground fine enough (5-10 µm) they posses a reasonable good pozzolanicity enhancing the durability of

concrete when replacing cement. Grinding can however be costly and calcined clay may thus be a better option.

Rice husk ash is also of interest as alternative pozzolan, but its availability seems to be concentrated in India and South-East Asia. However, this does not need to be a too big draw-back for international active businesses. It seems, however, that rice husk ash may benefit from some further processing before being used successfully in concrete as an active pozzolan enhancing both strength and durability.

Nano silica may give important improvement in concrete properties when added well dispersed as for instance as a suspension and not dried particles. However, the price is quite high and a cost/benefit ratio should be evaluated as well as the possibility of achieving similar properties by cheaper means.

Ground, recycled glass seems not to be of interest as a pozzolan for concrete since the activity is too slow, but it may be beneficial for rheological properties since it decreases the water demand of concrete. The pozzolanic activity might be increased by finer grinding, but the cost associated with this may be prohibiting.

6 REFERENCES

Al-Rawas A.A and A. W. Hago, **Evaluation of field and laboratory produced burnt clay pozzolans**, Applied CLAY Science 31, 2006, pp.29-35.

Al-Rawas A.A., A.W. Hago, T.C. Corcoran and K.M Al-Ghafri, **Properties of Omani artificial pozzolana (Sarooj)**, Applied CLAY Science 13, 1998, pp. 275-292.

American Society for Testing and Materials, **ASTM C311-05 Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete**, 2005.

American Society for Testing and Materials, **ASTM C618 Standard Specification for Coal Fly Ash and Raw or calcined Natural pozzolan for use in concrete** (Section 4, volume 04.02 October 2006)

Bensted, J. and P. Barnes, **Structure and Performance of Cements**, Second edition 2002, Spon Press London and New York

Bjönström J., A.Martenelli, A. Matic, L. Börjesson and I. Panas, **Accelerating effects of colloidal nano-silica for benefical calcium-silicate-hydrate formation in cement**, Chemical Physics Letters 392, 2004, p.242-248.

Byung-Wan J., K. Chang-Hyun and L. Jae-Hoon , **Characteristics of Cement Mortar with Nano-SiO₂ Particles**, ACI Materials Journal, Technical Paper, Title no. 104-M45, July-August 2007, p.404-407.

Chakhouk A, B. Samet and T. Minfi , **Study on the potential use of Tunisian clays as pozzolanic material,** Applied CLAY Science 33, 2006, p.79-88.

Chandaresekhar S., K.G. Satyanarayana, P.N. Pramada and P. Raghavan, **Review. Processing, properties and applications of reactive silica from rice husk – an overview**, Journal Material Science 38, 2003, p.3159-3168.

Chandaresekhar S., P.N. Pramanda and J. Majeed , **Effect of calcination temperature and heating rate on the optical properties and reactivity of rice husk ash**, Journal Material Science 41, 2006, p.7926-7933.

Chen G., H. Lee, K. L. Young and P.L. Yue, **Glass recycling in cement production – an innovative approach**, Waste Management 22, 2002, p.747-753.

Chindaparasirt P. and S. Rukzon, **Strength, porosity and corrosion resistance of ternary blend Portland cement, rice husk ash and fly ash mortar**, Construction and Building Materials, 2007, article in press.

Chindaparasirt P., P. Kanchanda, A. Sathonaowaphak and H.T. Cao, **Sulfate resistance of blended cements containing fly ash and rice husk ash**, Construction and Building Materials 21, 2007, p. 1356-1361.

Collepardi M., S. Collepardi, U.Skarp and R. Troli, **Optimization of Silica Fume, Fly Ash and Amorphous Nano-Silica in Superplasticized High-Preformance Concrete**, Proceedings of the eighth CANMET/ACI International conference on Fly Ash, Silica Fume, Slag and Natural pozzolans in Concrete, SP-221-30 V.M. Malhotra; 2004, p.495-505.

Cook D.J., **Calcined clay, shale and other soils**, Cement Replacement Materials, Concrete Technology and Design, Vol. 3, Editor: Swamy, R.N., Surrey University Press, England, 1985, pp. 40-71.

Coutinho J. Sousa, **The combined benefits of CPF and RHA in improving the durability of concrete structures**, Cement and Concrete Research 25, 2003, pp. 51-59.

Dahl P.A., H. Justnes, G. Norden, and O. Hyrve, **Lightweight Aggregate Fines as Pozzolanic Additive for High-Performance Concrete**, Proceedings of the ninth CANMET/ACI International conference on Fly Ash, Silica Fume, Slag and Natural pozzolans in Concrete, vol.1, SP-242. Warszawa: V.M. Malhotra; Mai 2007, pp.333-350.

Detwiler R.J., J.I. Bhatty, G. Barger and E.R. Hansen , **Durability of Concrete Containing Calcined Clay**, Concrete International, 2001, pp.43-47.

Diamond S., J.L. White and W.L Dolch, **Transformation of Clay Minerals by Calcium Hydroxide Attack**, Clays and Clay Minerals, 12th National Conference Atlanta, GA, 1963, Proceeding 1963, pp.359-379.

Feng Q., H. Yamamichi, M. Shoya and S. Sugita**, Efficiency of highly active rice husk ash on the high-strength concrete**, Proceedings of the 11th International Congress on the Chemistry of Cement (ICCC), Durban South Africa, 2003, pp.816-822.

Fernandez R., K. Scrivener, E. Gallucci and F. Marirena, **Calcined clay as a reactive pozzolan for cement substation**, Extended abstracts, 27th Cement and Concrete Science Meeting, Royal Holloway (London), September 2007.

Forrester J.A., **Burnt clay pozzolans**, Proceedings of Meeting on Small-Scale Manufacture of Cement Materials, 1974, Intermed Technol. Publ., London, 1975, pp.53-59.

Genesan K., K. Rajagopal and K. Thangavel, **Rice husk ash blended cement: Assessment of optimal level of replacement for strength and permeability properties of concrete**, Construction and Building Materials, 2007, article in press.

Giaccio G., G. Rodriguez de Sensale and R. Zerbino, **Failure mechanism of normal and high-strength concrete with rice-husk ash**, Cement & Concrete Composites 29, 2007, pp. 566-574.

He C., B. Osbæck, and E. Makovicky, **Pozzolanic reactions of six principal clay minerals: Activation, reactivity assessments** a**nd technological effects**, Cement and Concrete Research 25, 1995, pp. 1691-1702.

Johansen S. and P. J. Andersen, **Pozzolanic activity of calcined moler clay**, Cement and Concrete Research 20, 1990, pp. 447-452.

Justnes H. and T. Østnor, **Pozzolanic, Amorphous Silica Produced from the Mineral Olivine**, Proceedings of the seventh CANMET/ACI International conference on Fly Ash, Silica Fume, Slag and Natural pozzolans in Concrete, vol.2, SP-199. Chennai (Madras) India, V.M. Malhotra; July 2001. pp.769-782.

Justnes H., **Condensed silica fume as a cement extender**, Structure and Performance of Cements, Second edition 2002, Spon Press London and New York, pp.399-408.

Justnes H., **Hydraulic binders based on condensed silica fume and slaked lime**, Proceedings of the ninth International Congress on the Chemistry of Cement, Volume III Advances in Portland, Blended, Special and New Cements, New Delhi, India, 1992. pp. 284-290.

Klingstedt G., Fjällberg and I. Falkenby, **Utilization of glass filler in concrete making**, Proceedings Nordic Concrete Research Meeting, Göteborg 1993, pp.173-175.

Li H., H. Xiao, J. Yuan and J. Ou, **Microstructure of cement mortar with nano-particles**, Composites Part B: Engineering 35, 2004, pp.185-189.

Malhotra S.K. and N.G. Dave, **Investigations into the effect of addition of flyash and burnt clay pozzolana on certain engineering properties of cement composites**, Cement & Concrete Composites 21, 1999, pp.285-291.

Mielenz R., L. Witte and O. Glantz, **Effect of calcination on natural pozzolans**, Symposium in use of Pozzolanic materials in mortars and concretes, ASTM Special Technical Publication No.99, pp.43-92.

Miza, H. Wajahat and Al-Noury, I. Soliman **Powdered lightweight aggregate as a cement replacement material**, The International Journal of Cement Composites and Lightweight Concrete, Volume 10, No.3,1988, pp.171-173.

Moropoulou A., A. Bakolas and E. Aggelakopoulou, **Evaluation of pozzolanic activity of natural and artificial pozzolans by thermal analysis**, Thermochimica Acta 420, 2004, pp.135-140.

Müller, Christian Jörg, **Pozzolanic activity of natural clay minerals with respect to environmental geotechnics**, Doctor of Technical Science Diss.ETH No. 16299, Zurich 2005, 125 pp.

NS-EN 13263-1, 1.edition, October 2005.

Qing Y., Z. Zean, K. Deyu and C. Rongshen , **Influence of nano-SiO$_2$ addition on properties of hardened cement paste as compared with silica fume**, Construction and Building Materials 21, 2007, pp.539-545.

Rodriguez de Sensale G., **Strength development of concrete with rice husk ash**, Cement & Concrete Composites 28, 2006, pp. 158-160.

Sabir B.B. et al, **Metakaolin and calcined clay as pozzolans for concrete: a review**, Cement & Composites 23, 2001, pp.441-454.

Saraswathy V. and Song Ha-Won, **Corrosion performance of rise husk ash blended conctete**, Construction and Building Materials 21, 2007, pp.1779-1784.

Schwartz N., M. DuBois and N. Neithanath, **Electrical concuctivity based characterization of plain and coarse glass powder modified cement pastes**, Cement & Concrete Composites 29, 2007, pp. 656-666.

Schwarz N., M. DuBois and N. Neithalath, **Characterizing Cement Pastes Incorporating Two High Silica Fine Materials using Electrical Impedance**, Proceedings of the ninth CANMET/ACI International conference on Fly Ash, Silica Fume, Slag and Natural pozzolans in Concrete, vol.1, SP-242-20. Warszawa: V.M. Malhotra; Mai 2007, pp.253-266.

Shao Y., T. Lefort, S. Moras and D. Rodriguez, **Studies on concrete containing ground waste glass**, Cement and Concrete Researtch 30, 2000, pp.91-100.

Shayan A. and A. Xu, **Value-added utilization of waste glass in concrete**, Cement and Concrete Researtch 34, 2004, pp.81-89.

Shi C., Y. Wu C. Riefler and H. Wang, **Characteristics and pozzolan reacticity of glass powders**, Cement and Concrete Researtch 35, 2005, pp.987-993.

Shi, Caijun, **An overview on the activation of reactivity of natural pozzolans**, Canadian Journal of Civil Engineering, Volume 28, Number 5, 2001, pp.778-786.

Shih Jeng-Ywan, Ta-Peng Chang and Tien-Chin Hsiao, **Effect of nanosilica on characterization of Portland cement composite**, Materials Science and Engineering A 424, 2006, pp.266-274.

Souza P.S.L.and D.C.C.D. Molin **Viability of using calcined clays, from industial-products, as pozzolans of high reactivity**, Cement and Concrete Research 35, 2005, pp.1993-1998.

Vedalakshmi R., A. Sundara Raj, S. Srinivasan and K. Ganesh Babu, **Quantification of hydrated cement products of blended cements in low and medium strength concrete using TG and DTA technique**, Thermochimica Acta 407, 2003, pp.49-60.

Wada I., T. Kawano, M. Kawakami and N. Maeda, **Effect of Highly Reactive Rice Husk Ash on Durability of Concrete and Mortar**, Proceedings of the Fifth CANMET/ACI International conference on Durability of Concrete, vol. I, SP-192, Barcelona Spain, 2000, pp. 205-222.

Yamamichi H., F. Qingge and S. Sugita, **Some Properties of Concrete with Highly Active Rice Husk Ash**, Proceedings of the sixth CANMET/ACI International conference on Durability of Concrete, SP-212, 2003, pp. 891-906.

Yogananda M.R. and K.S. Jagadish, **Pozzolanic Properties of Rice Husk Ash, Burnt Clay and Red Mud**, Building and Enviroment, Vol. 23, No. 4, 1988, pp.303-308.

Zhang Min-Hong, **Microstructure and Properties of High Strength Lightweight Concrete**, Dr.ing. Dissertation 1989:51, The Norwegian Institute of Technology Division of Building Materials Trondheim, Norway, November 1989.