



**EXPERIMENTAL STUDY ON REACTIVITY OF PYROCLASTIC FLOW  
DEPOSIT CALLED SHIRASU AND ITS PRACTICAL USE AS  
CEMENTITIOUS MATERIAL**

Doctoral Thesis

by

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Kagoshima, Japan  
2010-2013



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A thesis submitted in partial fulfillment of the requirements for the degree of

**Doctor of Philosophy**

in

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Department of Ocean Civil Engineering

Graduate School of Science and Engineering

Kagoshima University

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2010-2013

## **DECLARATION**

I hereby declare that the thesis work entitled “**EXPERIMENTAL STUDY ON REACTIVITY OF PYROCLASTIC FLOW DEPOSIT CALLED SHIRASU AND ITS PRACTICAL USE AS CEMENTITIOUS MATERIAL**” Submitted to Kagoshima University for the award of the degree of Doctor of Philosophy in Material Science and Production Engineering, is a bonafied record of the work carried out under the guidance of Dr. Koji Takewaka, Professor, Department of Ocean Civil Engineering, Kagoshima University and that no part of this work has been presented earlier for any Degree, Diploma, Fellowship or any other similar titles to any other University or Institution.

Dhruva Narayana Katpady

## Abstract

Cement industry produces about 5% of global man made CO<sub>2</sub> emissions and its production process also releases volatile heavy metals which are hazardous in nature. Cement used in concrete construction and pavement materials in practice also leaches out harmful heavy metals and other chemicals. Utilization of pozzolans in concrete can solve the problems involved in the use of cement in concrete. Pozzolans not only improve quality of concrete and extend service life of structures but also reduce CO<sub>2</sub> emission significantly. In the research, unused natural resource called Shirasu is used in production of new construction materials.

Shirasu is a pyroclastic flow deposit abundantly deposited due to a big pyroclastic flow occurred twenty to hundred thousands of years ago in the southern part of Kyushu Island of Japan. Past researches have been done on the potential use of Shirasu as fine aggregate in concrete, which is called as “Shirasu concrete”. Shirasu concrete has proved to be durable in harsh environment highly resistant to sulfate attack and chloride ingress. Shirasu as fine aggregate is also confirmed to have long term pozzolanic reaction due to high fine particle fraction. Based on these facts, it is expected that Shirasu as cement replacement material may have similar performance as Shirasu concrete. Hence, performance of Shirasu is examined as binder material and also as fine aggregate in different construction materials.

Utilization of unused natural resources like volcanic ash and recycling and reusing of industrial wastes as construction material is the major aim of the research. Shirasu is used as one of the binders in mortar and also as fine aggregate from the view points of effective use of unused natural resource and CO<sub>2</sub> free material. In this study, following three types of new materials are developed in which Shirasu and additionally, recycled wastes like gypsum and fly ash are used;

- (1) Study on pozzolanic reactivity of Shirasu as a cement replacement material by using fine particles of Shirasu (size under 150 $\mu$ m) with different replacement ratios.
- (2) The study on permeable pavement using Shirasu as fine aggregate with recycled gypsum from used plasterboards as one of the binders.
- (3) Geopolymer mortar with Shirasu of size under 75 $\mu$ m as aluminosilicate source, and mixture of NaOH and Na<sub>2</sub>SiO<sub>3</sub> solutions as alkaline activators to study the reactivity of Shirasu in polymerization reaction.

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Dhruva Narayana Katpady

*I dedicate this thesis to my parents for their love and affection and  
encouragement for success in my life*

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## **Chapter 1**

### **INTRODUCTION**

#### **1.1 General**

Concrete is a composite material composed of cement as binder and aggregates like sand and gravel. Cement is the main ingredient in concrete. The usage of concrete, worldwide, is twice as much as steel, wood, plastics, and aluminum combined. Hence, demand for cement also increases. The manufacture and use of concrete produce a wide range of environmental and social consequences. Some are harmful, depending on circumstances. A major component of concrete is cement, which similarly exerts environmental and social effects. The cement industry is one of the three primary producers of carbon dioxide, a major greenhouse gas. The other two are the energy production and transportation industries. The presence of some substances in concrete, including useful and unwanted additives, can cause health concerns due to toxicity and radioactivity. Recently, utilization of pozzolans in concrete has attracted the attention as a solution to the problems of traditional concrete. Pozzolans have the potential of improving the quality of concrete and also solve the environmental problems posed by traditional concrete.

The search for alternative binders or cement replacement materials had been continued for last decade. Comprehensive research had been carried out in the past on the use of fly ash, blast furnace slag, and silica fumes etc. as the cement replacement materials.



The volcanic ash, pumicite, fly ash etc. are pozzolanic materials because of their reaction with calcium hydroxide liberated during the hydration of cement. The amorphous silica present in the pozzolans reacts with free lime to form cementitious materials. They impart not only technical advantages to concrete but also enable large quantity of cement replacement to be achieved. These materials can also improve the durability of concrete, rate of gain in strength and reduce the heat liberated during hydration.

## **Cement**

Portland cement is widely used as binder in concrete. Cement is an important construction ingredient around the world, and as a result, cement production is a significant source of global carbon dioxide (CO<sub>2</sub>) emissions. Cement is produced in large, capital intensive production plants generally located near limestone quarries or other raw carbonate mineral sources as these sources are the principal raw materials used in the cement production process. Carbon dioxide is emitted as a by-product of clinker production, an intermediate product in cement manufacture, in which calcium carbonate (CaCO<sub>3</sub>) is calcinated and converted to lime (CaO), the primary component of cement [1]. Carbon dioxide is also emitted during cement production by fossil fuel combustion.

Cement industry accounts for around 5% of global carbon dioxide (CO<sub>2</sub>) emissions. Cement is the primary ingredient in concrete, which in turn forms the foundations and structures of the buildings we live and work in, and the roads and bridges we drive on. Concrete is the second most consumed substance on Earth after water. On average,

each year, three tons of concrete are consumed by every person on the planet. Concrete is used globally to build buildings, bridges, roads, runways, sidewalks, and dams. Cement is indispensable for construction activity, so it is tightly linked to the global economy. Cement production is growing by 2.5% annually, and is expected to rise from 2.55 billion tons in 2006 to 3.7-4.4 billion tons by 2050. Though “cement” and “concrete” are often used interchangeably, concrete is actually the final product made from cement. The primary component of cement is limestone. To produce cement, limestone and other clay-like materials are heated in a kiln at 1400°C and then ground to form a lumpy, solid substance called clinker; clinker is then combined with gypsum to form cement. Cement manufacturing is highly energy – and – emissions intensive because of the extreme heat required to produce it. Producing a ton of cement requires 4.7 million BTU of energy, equivalent to about 400 pounds of coal, and generates nearly a ton of CO<sub>2</sub>. Given its high emissions and critical importance to society, cement is an obvious place to look to reduce greenhouse gas emissions.

The production of cement releases greenhouse gas emissions both directly and indirectly: the heating of limestone releases CO<sub>2</sub> directly, while the burning of fossil fuels to heat the kiln indirectly results in CO<sub>2</sub> emissions. The direct emissions of cement occur through a chemical process called calcination. Calcination occurs when limestone, which is made of calcium carbonate, is heated, breaking down into calcium oxide and CO<sub>2</sub>. This process accounts for about 50% of all emissions from cement production. Indirect emissions are produced by burning fossil fuels to heat the kiln. Kilns are usually heated by coal, natural gas, or oil, and the combustion of these fuels produces additional CO<sub>2</sub> emissions, just as they would in producing electricity. This represents

around 40% of cement emissions. Finally, the electricity used to power additional plant machinery, and the final transportation of cement, represents another source of indirect emissions and account for 5-10% of the industry's emissions.

In recent years, effective use of pozzolans as cement replacement materials in concrete are actively examined. Pozzolans impart technical advantages to concrete by improving the durability of concrete, rate of gain in strength and reduce the heat generated during hydration. In addition, as pozzolans enable large quantity of cement replacement to be achieved, they are not only expected to be used for improvement of quality of concrete but also for significant reduction in the CO<sub>2</sub> emissions.

### **Volcanic ash**

Volcanic ash is formed during explosive volcanic eruptions, phreatomagmatic eruptions and during transport in pyroclastic density currents. Physical and chemical characteristics of volcanic ash are primarily controlled by the style of volcanic eruption. The types of minerals present in volcanic ash are dependent on the chemistry of the magma from which it was erupted. Volcanic ash is high in silica (>69%) while other types of ash with an intermediate composition (e.g. andesite or dacite) have a silica content between 55-69%. Volcanic ash particles erupted during magmatic eruptions are made up of various fractions of vitric (glassy, non-crystalline), crystalline or lithic (non-magmatic) particles. Volcanic ash and other related deposits, such as tuff and pumice, constitute valuable materials for construction.

### **Pyroclastic flow**

A pyroclastic flow (also known scientifically as a pyroclastic density current) is a fast-moving current of hot gas and rock (collectively known as tephra), which reaches speeds moving away from a volcano of up to 700 km/h (450 mph). The gas can reach temperatures of about 1000°C. Pyroclastic flows normally hug the ground and travel downhill, or spread laterally under gravity. Their speed depends upon the density of the current, the volcanic output rate, and the gradient of the slope. They are a common and devastating result of certain explosive volcanic eruptions. Shirasu (“white sand” in Japanese), is a kind of pyroclastic flow deposit abundantly available in the southern part of Kyushu Island of Japan and is one of the unused natural resources. It has very high amount of volcanic glass in its mineral composition and regarded as a pozzolan capable of pozzolanic reaction.

### **Pozzolans**

The name Pozzolan comes from the town Pozzuoli, Italy. Ancient Romans (~100 B.C.) produced a hydraulic binder by mixing hydrated lime with soil (predominantly volcanic ash). Horasan mortar, mixing lime with finely divided burned clay, is extensively used by Ottomans. Nowadays, the word pozzolan covers a broad range of natural and artificial materials.

Pozzolan is a material that, when used in conjunction with Portland cement, contributes to the properties of the hardened concrete through hydraulic or pozzolanic activity, or both.

- Natural pozzolans: Volcanic ash, volcanic tuff, pumicite
- Artificial pozzolans: fly ash, silica-fume, granulated blast furnace slag

Pozzolan is siliceous or aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide  $\text{Ca(OH)}_2$  to form compounds possessing hydraulic cementitious properties. The benefits of pozzolan utilization in cement and concrete are threefold.

1. First is the economic gain obtained by replacing a substantial part of the Portland cement by cheaper natural pozzolans or industrial by-products.
2. Second is the lowering of the blended cement environmental cost associated with the greenhouse gases emitted during Portland cement production.
3. A third advantage is the durability improvement of the end product.

### **Pozzolan reaction**

Calcium hydroxide + Silica + Water  $\rightarrow$  “Calcium-Silicate-Hydrate” (C-S-H).

C-S-H provides the hydraulic binding property of the material.

### **Pozzolan reactivity**

Pozzolan reactivity is the degree or rate of reaction of pozzolan as binder in mortar or concrete. Reactivity is affected by following important factors

- 1)  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  content
- 2) The degree of amorphousness of its structure
- 3) Fineness of its particles

For chemical reaction, pozzolans must be amorphous or glassy in nature. Volcanic ash, volcanic tuff, fly ash, silica fume are all amorphous by nature. Clays contain high amounts of silica & alumina but have a crystalline structure. However, by heat treatment,

such as calcining around  $\sim 700\text{-}900^{\circ}\text{C}$  crystalline structure is destroyed and a quasi-amorphous structure is obtained.

Industrial wastes such as fly ash and also volcanic ash produced by natural phenomenon pose potential threat to environment and health. Handling of these wastes is a major problem. To reduce pollution and disposal problems of these industrial wastes, there is an urgent need to develop useful building materials from them. In recent years, effective use of pozzolans as cement replacement materials in concrete are extensively examined. Pozzolans not only improve quality of concrete but also significantly reduce  $\text{CO}_2$  emissions. Pozzolans as cement replacement materials have wide variety of applications in construction industry as they are potentially capable of improving the service life of concrete and contribute to sustainable environment and concrete. However, as lot of  $\text{CO}_2$  is emitted in the production process of the cement, reducing the cement content in concrete without any reduction in quality is effective in sustainability of concrete and environment. With this view, investigations were undertaken to produce cementitious binders by blending with Portland cement as well as by suitably proportioning.

## **1.2 Shirasu as Binder**

Shirasu is a pyroclastic flow deposit abundantly deposited due to a big pyroclastic flow occurred twenty to hundred thousands of years ago in the southern part of Kyushu Island of Japan. Past researches have been done on the potential use of Shirasu as fine aggregate. The concrete made with Shirasu as fine aggregate is named as “Shirasu concrete”. Shirasu concrete has proved to be durable in harsh environment in terms of

chemical attack and high temperature conditions. Shirasu concrete has high resistance to sulfate attack and chloride ingress. Shirasu as fine aggregate is also confirmed to have long term pozzolanic reaction due to high fine particle fraction. Pozzolanic characteristics of Shirasu improve the quality of concrete, increases durability, reduce the total heat of hydration, and can play an important role as sustainable concrete material. From the point of view of potential utilization of unused natural resource and reduction of greenhouse emissions, it is important to study Shirasu as a cement replacement material and its contribution towards sustainable concrete. In the present experimental investigation, pozzolanic reactivity of Shirasu is examined by using fine Shirasu particles as cement replacement.

Details of experimental investigations done to exploit usage potential of Shirasu as concrete material have been presented with suggestions on optimum replacement levels and suitable water binder ratio (here-in-after called “W/B”) for accomplishment of best results. The study is concerned with comparing the engineering properties between Shirasu and fly ash mortars. Compressive strength and bending strength of mortar containing Shirasu and fly ash as binders are compared in order to study the reactivity of these pozzolans in mortar. Shirasu and fly ash are used as binder materials by making their fineness (Blaine specific surface) similar and testing for their relative performance, in terms of reactivity and strength. Similar conditions of Shirasu and fly ash (same fineness/ Blaine specific surface) help in easy and good comparison of their behavior in mortar and concrete.

### **1.3 Shirasu as Fine Aggregate and Recycled Plasterboards as Binder in Mortar for Permeable Pavement**

For centuries now gypsum has played a crucial role in construction. Often also referred to as drywall rock, plasterboard, or gypboard, gypsum drywall is a sheet of gypsum with a paper facing and backing of which contents are approximately 92% gypsum (calcium sulfate dehydrate  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), 7% paper, and 1% impurities and additives. Cement plants use large quantities of virgin gypsum. The gypsum is added to the “clinker” to control the setting time. Researches on using recycled gypsum showed positive results except that the paper caused problems.

Permeable pavements using Sand as fine aggregate and cement as binder is being practically used worldwide. However, in this research attempt has been made in using gypsum present in recycled plasterboards in partial replacement of cement. Crushed plasterboards are burnt at temperatures as high as  $180^\circ\text{C}$ . The product is  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$  which is used as binder, replacing cement partially. The above compound contains very little paper and advantageous. The original gypsum, in some adverse conditions produces hydrogen sulfides, when combines with water, which are harmful to environment. With this knowledge, original gypsum in plasterboards are converted to  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$  and used in experimentation.

Permeable pavement is made with Shirasu as fine aggregate and recycled gypsum as one of the binders. In the present study, compressive strength and permeability of mortar, in which Portland cement and the gypsum are used as binder, are carried out according



to set target values of  $3.8\text{N/mm}^2$  for compressive strength and  $5\times 10^{-5}\text{cm/s}$  permeability. The target values are based on experimental investigation done on commercial materials for good permeable pavement of promenade.

#### **1.4 Shirasu in Geopolymer**

Recently, geopolymer technology is known to be green technology where no cement is used in making concrete. Instead, pozzolans having high content of silica and alumina are used. These pozzolans are alkali activated and subjected to heat curing at high temperatures. Geopolymer develops strength at a very faster rate compared to traditional concrete. Lately, geopolymer technology attracted the attention as one of the  $\text{CO}_2$  free construction materials because of concrete free from cement. Extensive research is carried out on fly ash and metakaolin based geopolymer. Fly ash geopolymer is strong and durable and further studies are being carried on the durability and other aspects. Shirasu also shows pozzolanic reactivity similar to fly ash and is characterized by high content of silica and alumina. Hence, potential of Shirasu needs to be exploited in geopolymer technology where Shirasu is used as aluminosilicate source.

The present investigation is an attempt to study the performance of geopolymer with Shirasu as aluminosilicate source. The behavior of Shirasu geopolymer is compared with that of geopolymer mortars prepared with fly ash which is considered as control in this study. Past researches have proved that fly ash geopolymer are generally more strong and durable. As Shirasu is rich in silica and alumina it can be potentially used in Geopolymer and also based on facts available that Shirasu concrete is durable in hot

spring environments where temperatures rise up to 130<sup>0</sup>C. With this knowledge, Shirasu geopolymer with different W/B is tried. The alkali activated specimens are subjected to different temperatures and the compressive strengths tests are carried out to compare between Shirasu and fly ash geopolymers. The porosity tests on each geopolymer mortar are also done to study the behavior of internal structure of geopolymer mortar. As Shirasu and fly ash have different characteristics, an attempt to study the strength development of mortars and to obtain optimum strength is done assuming silica to hydroxide ratio (here-in-after called “Si/OH”) in the mix proportion to be one of the important parameters.

## **Chapter 2**

### **CHARACTERISTICS OF SHIRASU**

#### **2.1 General**

A kind of the volcanic ash called "Shirasu", which was abundantly deposited due to a big pyroclastic flow in the southern part of Kyushu Island, Japan, in 20 to 100 thousand years ago, is one of the unused natural resources. Shirasu is sandy but porous material with large amount of very fine particles. It has about 80% density of that of sea sand and three times higher water absorption capacity when compared to sea sand. It also has high quantity of volcanic glasses in its mineral compositions and has been confirmed to show pozzolanic reaction [2]. The quantity of volcanic glasses in Shirasu's composition is approximately 80%. Therefore, it should be an important subject to investigate Shirasu as alternative material to cement and/or aggregates for concrete. Takewaka and co-researchers have made a series of investigation on the applicability of Shirasu in Shirasu concrete where Shirasu is used as fine aggregate. They have reported the mix proportion and the strength characteristics of Shirasu concrete [3] and also clarified that Shirasu concrete has shown long-term durability concerning to salt attack, sulfate attack, alkali aggregate reaction, and etc. [2][4].

Now, Shirasu concrete is successfully applied to the concrete foundation for piers constructed in hot spring environment. Continuous deterioration monitoring on bridge piers made of Shirasu concrete were carried out. The Shirasu concrete could withstand

low pH values of 2.9 and high concentrations of sulfates in hot spring environment. Pozzolanic characteristics of Shirasu improve the quality of concrete, increases durability, reduce the total heat of hydration, and can play an important role as sustainable concrete material. From the point of view of potential utilization of unused natural resource and reduction of greenhouse emissions, it is important to study Shirasu as a cement replacement material and its contribution towards sustainable concrete.

## **2.2 Natural Condition of Shirasu**

Shirasu is one of famous volcanic products in Kagoshima Prefecture and defined as a non-welded part of pyroclastic flow deposits.



Fig. 2.1 Natural condition of Shirasu deposit

Shirasu was deposited several thousand years ago and is one of the unused natural

resources. Shirasu deposit seems to be rock because of strong binding effect between Shirasu particles. However, once the rock is scratched, Shirasu changes to sandy condition. Fig. 2.1 shows the natural deposit of Shirasu. More than 60 billion cubic meters of Shirasu cover is found in Kagoshima Prefecture. The deposition of Shirasu due to pyroclastic flow is spread over a large area at different locations depending on the density of flow and the terrain.

### **2.3 Types and Properties of Shirasu**

Shirasu is said to have deposited due to a large scale pyroclastic flow that occurred millions of years ago. The earliest pyroclastic flow that occurred in Kagoshima Prefecture is nearly 3 million years old. Among the many pyroclastic flows, Kakuto pyroclastic flow occurred 100 thousand years ago, while Ata pyroclastic flow about 80 thousand years ago, Tsumaya pyroclastic flow about 25 thousand years ago and Ito pyroclastic flow occurred about 22 thousand years ago. Especially, Ito pyroclastic flow deposit is widely distributed in the mainland of Kagoshima Prefecture.

Ito pyroclastic flow was generated by a large scale eruption of Aira caldera aging 22000 years. The upper part of the Shirasudaichi and surrounding Kagoshima city, is mainly the deposits of Ito pyroclastic flow.

The different types of Shirasu deposit available in Kagoshima Prefecture of Japan at different locations based on density current and origin are shown in Table 2.1.

Table 2.1 Properties of different types of Shirasu based on location of deposit

Type of Shirasu/location	Density of surface-dry state (g/cm <sup>3</sup> )	Absorption capacity ratio (%)	Fineness modulus	Fine powder ratio (%)
Kagoshima shi	2.06	11.31	1.53	21.9
Yoshida	2.22	4.29	1.57	20.54
Kiire	2.16	4.2	1.68	16.64
Makurazaki	2.24	3.11	1.18	23.4
Kaseda	2.16	8.48	1.12	27.55
Kawanabe	2.24	2.51	1.26	24.44
Higashi Ichiki	2.24	3.6	1.56	20.02
Koriyama	2.22	6.03	1.73	20.6
Ijuin	2.24	3.23	1.62	20.37
Matsumoto	2.22	3.07	1.63	24.46
Hioshi	2.24	2.67	1.6	21.3
Fukiage	2.19	4.29	1.43	26.63
Kimpo	2.22	3.07	1.14	19.48
Hiwaki	2.27	3.83	1.69	16.35
Tsuruta	2.25	3.61	1.44	26.41
Satsuma	2.23	3.82	1.52	24.06
Iriki	2.3	2.6	1.57	18.64
Izumi	2.22	5.07	1.21	25.52
Mizobe	2.16	6.4	1.83	17.91
Yokogawa	2.2	6.54	1.57	20.11
Kirishima	2.19	4.91	1.68	20.79
Fukuyama	2.11	9.62	2.09	20.86
Tarumizu	2.18	5.46	1.43	24.89
Takarabe	2.18	4.77	1.68	21.49
Shibushi	2.2	4.02	1.27	27.36
Sueyoshi	2.21	4.28	1.51	25.04
Matsuyama	2.24	3.11	1.5	24.53
Kihoku	2.17	3.62	1.87	22.35
Ariake	2.19	6.72	1.47	25.45
Takayama	2.19	4.17	1.5	23.36
Aira	2.17	2.88	1.37	24.8

Shirasu is angular and porous material. Fig. 2.2 of microscopic condition of Shirasu confirms the porous nature of Shirasu. The size distribution of Shirasu particle is shown in Fig. 2.3. The physical characteristics of some Shirasu compared to sea sand are shown in Table 2.2. Shirasu has about 80% of the density and nearly three times of the absorption capacity as compared with the sea sand. The general chemical characteristics

of Shirasu are shown in Table 2.3. Shirasu contains high percentage of silica and alumina. These chemical components almost constitute volcanic glasses. The quantity of volcanic glasses in Shirasu's composition is approximately 80%.

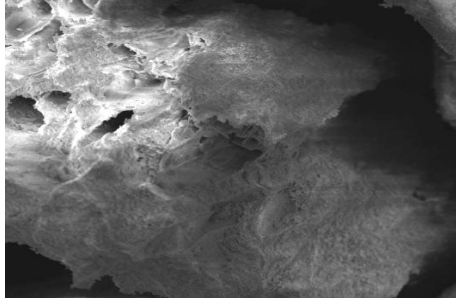


Fig. 2.2 Microscopic condition of Shirasu particle

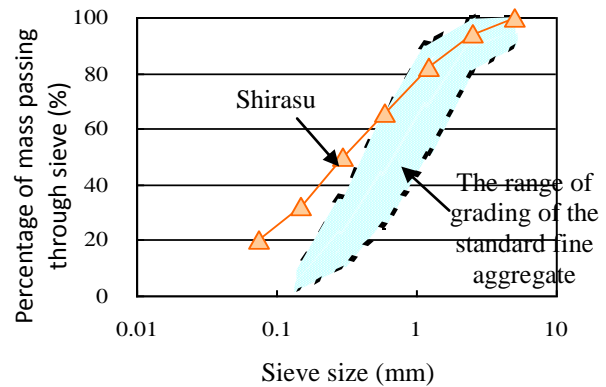


Fig. 2.3 Size distribution of Shirasu particles

Table 2.2 Physical characteristics of some Shirasu compared to sea sand

Physical Characteristics	SHIRASU 1	SHIRASU 2	SHIRASU 3	Sea sand
Density of surface-dry state ( $\text{g/cm}^3$ )	2.15	2.20	2.16	2.5~2.7
Absorption capacity ratio (%)	6.74	6.54	8.48	1~3
Content ratio of the fine powder (%)	23.11	20.11	27.55	~5.0
Fineness modulus of aggregate (F.M.)	1.60	1.75	1.12	2.0~3.5
Solid volume ratio (%)	56.09	55.11	50.97	55~65

Table 2.3 General chemical composition of Shirasu

Chemical composition	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$
content ratio (%)	76.60	12.20	1.48	1.08	3.43	3.54

## **Chapter 3**

### **POZZOLANIC REACTIVITY OF SHIRASU**

#### **3.1 Shirasu of Particle Size under 150 $\mu$ m as Binder**

##### **3.1.1 General**

Researches have been carried out in the past on the use of Shirasu as fine aggregate in concrete which is called as “Shirasu concrete”. Shirasu concrete is highly durable in harsh environments and Shirasu showed long term pozzolanic reactivity. Shirasu concrete used in construction of bridge piers in hot spring environment also showed high resistance to sulfate attack and low pH conditions. It is expected that Shirasu as binder (cement replacement material) in concrete has the same effect as Shirasu concrete. Therefore, in the present study, fine particles of Shirasu ( $\sim 150\mu\text{m}$ ) is used as cement replacement material in mortar to study its pozzolanic reactivity. Two types of Shirasu namely Shirasu 1 (S1) and Shirasu 2 (S2) and two types of fly ash namely Fly ash 1 (F1) and Fly ash 2 (F2) are used as binders in mortar.

Fly ash as a pozzolan is known to be highly reactive. Fly ash as cement replacement material also improves the workability of concrete and reduces the demand of water requirement. The short term and long term strength of concrete using fly ash as cement replacement material is said to be higher than ordinary concrete where ordinary Portland cement (here-in-after called “OPC”) alone is used as binder. Therefore, in this



experimental study, reactivity of Shirasu in mortar is compared with the fly ash mortars and ordinary mortars with OPC as control specimen. Fine particles of Shirasu and fly ash are used as cement replacement materials. Shirasu and fly ash partially replace cement as binders in different percentages of the amount of cement. Prism specimens of 4cm\*4cm\*16cm were made with three types of W/B, i.e., 40%, 50% and 60%. The replacement ratios of Shirasu/fly ash were fixed at 10%, 20% and 30% for each W/B. The specimens are tested for compressive strength and bending strength for normal water curing periods of 1, 3, 7, 14, 28, 91, 270 and 365 days.

### **3.1.2 Materials**

1. Binders:

Ordinary Portland cement is used. Shirasu/fly ash as binders (cement replacement materials) with different replacement percentages from total cement content is used.

2. Sand:

River sand is used as fine aggregate

3. Super Plasticizer (SP): Super plasticizers are used only in case of mortars having low workability (low flow value). They are used to equalize the flow of mortars with different water to binder ratios.

### **Preliminary tests on Shirasu**

Preliminary tests conducted on two types of Shirasu were specific gravity, water absorption, mortar flow test and setting time test.

***Specific Gravity:***

Specific gravity test was conducted as per JIS A 1109-2006 standards specifications.

The method involved is same as in the case of specific gravity of cement.

***Water absorption:***

Shirasu particles are highly porous in nature. Introduction of Shirasu in the mix may alter the actual water-binder ratio for mortar. Hence water absorption is a key factor in proportioning of ingredients in concrete. Water absorption test is carried out as per JIS A 1109 2.3.

***Mortar Flow Test:***

Flow Test is conducted for all designed mix proportions according to JIS specifications for all types of mortar, i.e., for OPC and mortar containing fly ash or Shirasu as binders. Fig. 3.1 shows the flow values of Shirasu and fly ash mortars for different water binder ratio and replacement levels. Shirasu mortars have lesser flow values compared to the fly ash mortars. Shirasu particles are porous and absorb considerable amount of water while mixing. This reduces the flow characteristics of fresh mortar. Similar effect is illustrated in the results which show that as the replacement ratio of Shirasu increases the flow decreases. On the other hand, fly ash as binder is known to increase the workability of concrete due to “ball bearing effect” of smooth and spherical fly ash particles.

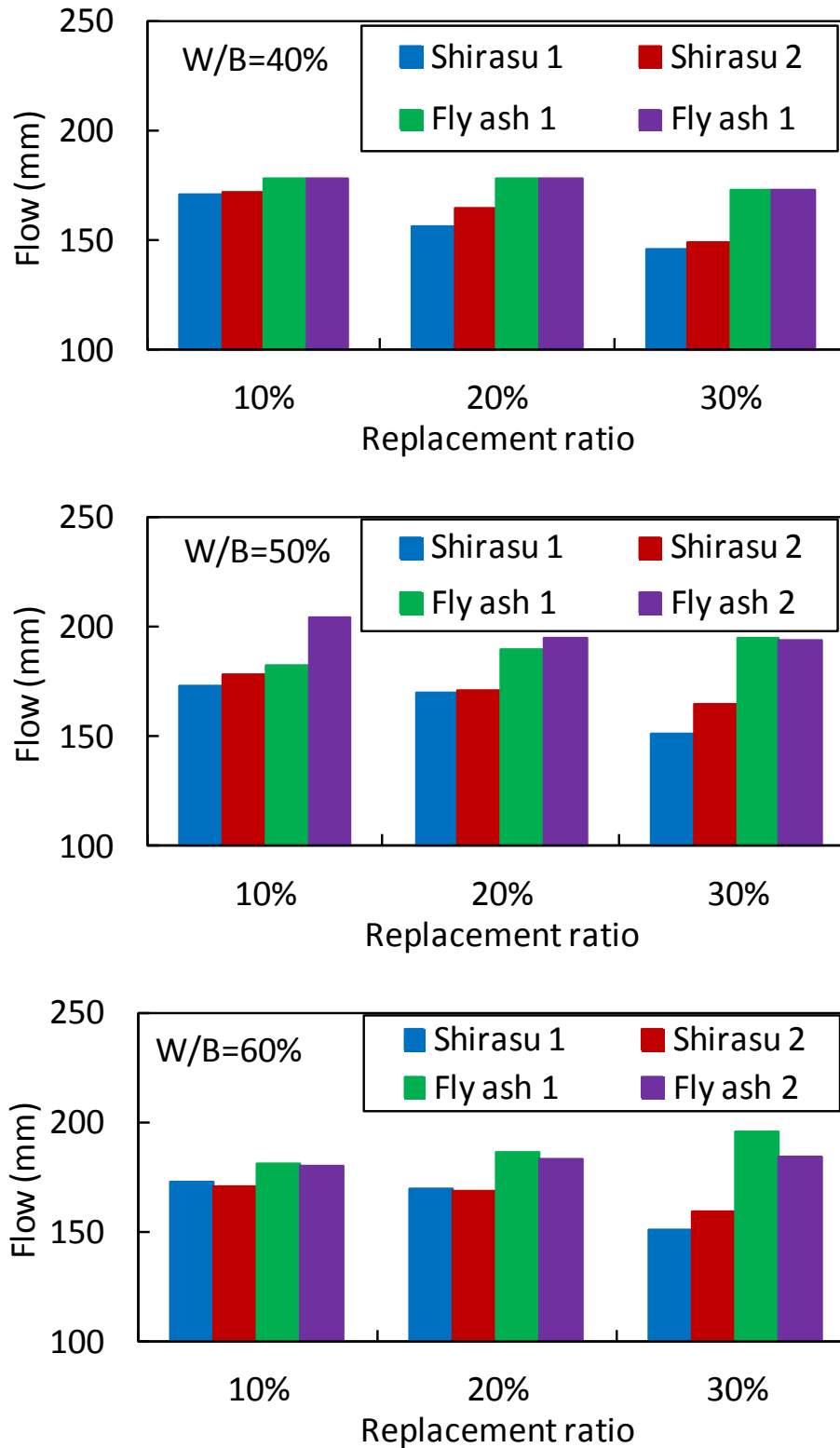


Fig. 3.1 Mortar flow values for different water binder ratio and replacement levels

### ***Setting Time Test:***

Initial setting time and final setting time are determined for mortar with Shirasu as binder.

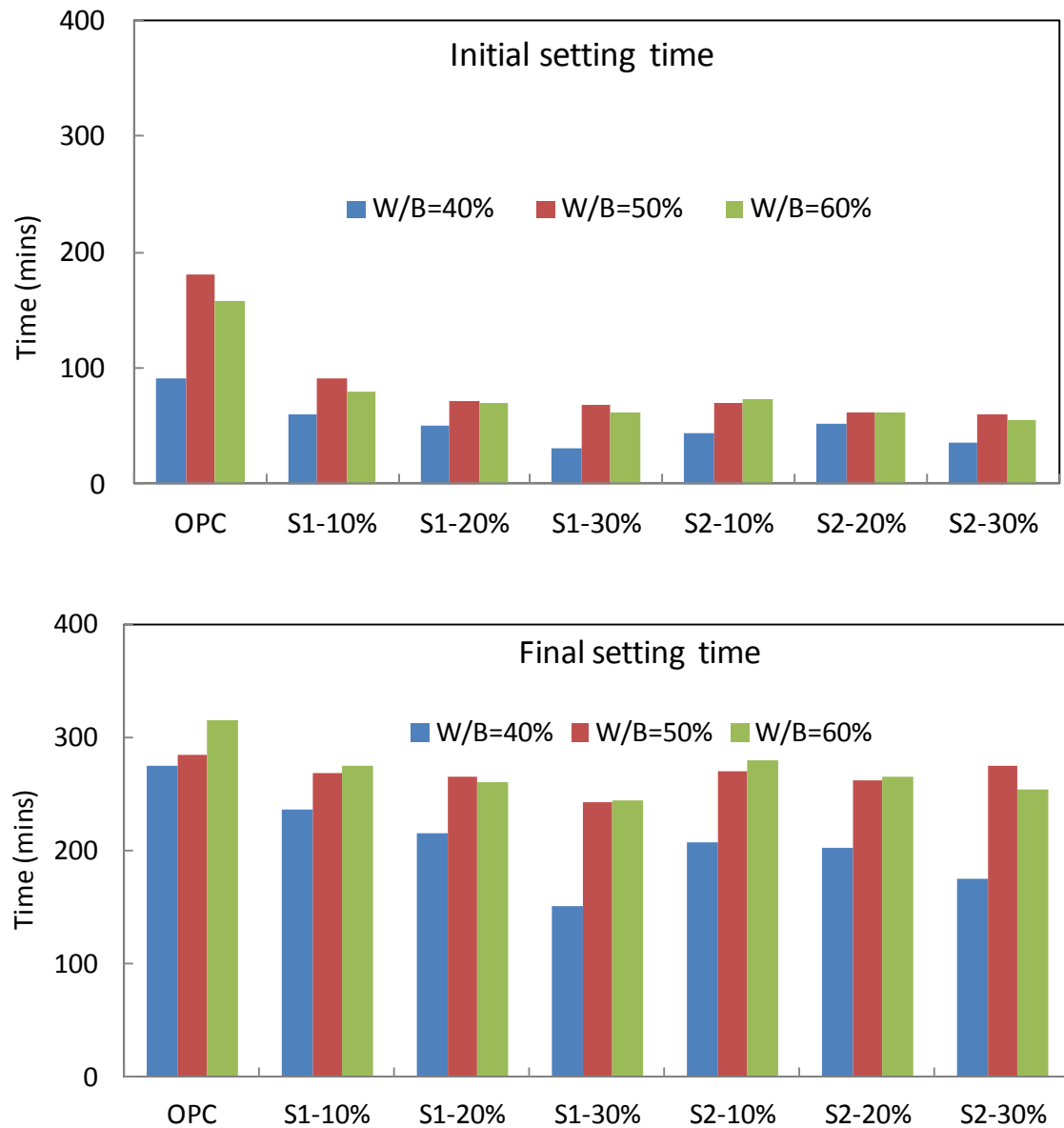


Fig. 3.2 Setting time of Shirasu mortars

Fig. 3.2 shows the initial and final setting time of Shirasu mortars with different W/B

and replacement ratios (For ex. S1-10% means Shirasu 1 replacing cement by 10%). The results of setting time show that the rate of stiffening of Shirasu mortar is higher than OPC (initial setting time graph). The hardening rate of Shirasu mortar is also higher compared to OPC. This is because of the fact that Shirasu absorbs water in the mix and stiffens the mixture more than in the case of OPC.

### 3.1.3 Physical and Chemical Characteristics of Binders

Characteristics of two types of Shirasu used are shown in Table 3.1. Both types of Shirasu have high amount of silica and alumina in their chemical composition. Shirasu 1 and Shirasu 2 have specific gravities of 2.43 and 2.39 respectively. Especially, the water absorption capacity of both Shirasu is as high as 8.15% and 7.52%.

Table 3.1 Characteristics of Shirasu used

Characteristics	Shirasu 1	Shirasu 2
SiO <sub>2</sub> (%)	67.65	69.18
Al <sub>2</sub> O <sub>3</sub> (%)	14.19	14.41
Fe <sub>2</sub> O <sub>3</sub> (%)	2.47	2.92
MgO (%)	0.71	0.71
CaO (%)	2.58	3.23
Ignition loss	1.93	1.89
Specific gravity	2.43	2.39
Water absorption	8.15%	7.52%

Two types of fly ash are used in this study and the physical and chemical characteristics of fly ash used are shown in Table 3.2. Similar to Shirasu, both fly ashes have high amount of silica and alumina. Fly ash particles are fine with Blaine specific surface area of around 3690cm<sup>2</sup>/g to 3990cm<sup>2</sup>/g.

Table 3.2 Characteristics of fly ash used

Characteristics	Fly ash 1	Fly ash 2
SiO <sub>2</sub> (%)	66.62	63.3
Al <sub>2</sub> O <sub>3</sub> (%)	22.41	22.41
Fe <sub>2</sub> O <sub>3</sub> (%)	5.74	5.74
MgO (%)	1.01	1.01
CaO (%)	1.93	1.93
Ignition loss	2	2.7
Specific gravity	2.22	2.25
Blaine specific surface area (cm <sup>2</sup> /g)	3690	3990

### 3.1.4 Mix Proportions and Curing Method

Mortars with water binder ratios of 40%, 50% and 60% and for each W/B, replacement ratios of 10%, 20% and 30%, are prepared and, prism mortar specimens with 4 square centimeter cross section and 16 centimeter long have been casted. The mix proportions of Shirasu and fly ash mortars are shown in Table 3.3 and Table 3.4.

Table 3.3 Mix proportion for Shirasu mortar (unit weight, kg/m<sup>3</sup>)

W/B	Replacement ratio		Water	Cement	Shirasu	Sand
40%	10%	Shirasu 1	291	656	73	1241
		Shirasu 2	291	656	73	1241
	20%	Shirasu 1	288	575	144	1241
		Shirasu 2	288	575	144	1241
	30%	Shirasu 1	284	497	213	1241
		Shirasu 2	284	497	213	1241
50%	10%	Shirasu 1	290	522	58	1373
		Shirasu 2	290	522	58	1373
	20%	Shirasu 1	287	459	115	1373
		Shirasu 2	287	459	115	1373
	30%	Shirasu 1	283	397	170	1373
		Shirasu 2	283	397	170	1373
60%	10%	Shirasu 1	285	427	47	1478
		Shirasu 2	285	427	47	1478
	20%	Shirasu 1	282	376	94	1478
		Shirasu 2	282	376	94	1478
	30%	Shirasu 1	279	325	139	1478
		Shirasu 2	279	325	139	1478

Table 3.4 Mix proportion for fly ash mortar (unit weight, kg/m<sup>3</sup>)

W/B	Replacement ratio		Water	Cement	Fly ash	Sand
40%	10%	Fly ash 1	290	653	73	1241
		Fly ash 2	291	654	73	1241
	20%	Fly ash 1	285	570	142	1241
		Fly ash 2	286	572	143	1241
	30%	Fly ash 1	280	490	210	1241
		Fly ash 2	281	493	211	1241
50%	10%	Fly ash 1	289	520	58	1373
		Fly ash 2	289	521	58	1373
	20%	Fly ash 1	284	455	114	1373
		Fly ash 2	285	456	114	1373
	30%	Fly ash 1	280	392	168	1373
		Fly ash 2	281	394	169	1373
60%	10%	Fly ash 1	284	425	47	1478
		Fly ash 2	284	426	47	1478
	20%	Fly ash 1	280	373	93	1478
		Fly ash 2	280	374	93	1478
	30%	Fly ash 1	276	322	138	1478
		Fly ash 2	277	323	138	1478

All the mix proportions are maintained at unit weight consistency. Along with the



Shirasu and fly ash mortars, OPC mortars are also prepared with W/B of 40%, 50% and 60% with mix proportion of unit weight consistency. For each water binder ratio, replacement levels of 10%, 20% and 30% are set. After casting, the specimens are normal water cured for predetermined curing periods of 1, 3, 7, 14, 28, 91, 270 and 365 days. The prism specimens are used for bending strength test and the split specimens are then used for compressive strength testing.

### **3.1.5 Results and Discussion**

#### **Strength of mortars with material age for W/B=40%**

The results of compressive strength for W/B=40% with replacement ratios of 10%, 20% and 30% (illustrated in Fig. 3.3, 3.4 and 3.5), show that mortar containing Shirasu as binder has higher early strength than other mortars (1-7 days). Mortar with Shirasu has high initial setting time and final setting time due to its higher water absorption characteristics and porous nature. Hence the mortar hardens at a faster rate. When they are mixed with water, they absorb water and slightly alter the water content in the mix.

The compressive strength of Shirasu mortars decrease with the increase in replacement ratio. As the hydration of cement is quicker, rate of gain in strengths for mortar with low levels of replacements is higher at early stages of curing. Between 28 days and 91 days of curing period, there is a difference in trend, where compressive strength of Shirasu mortar is almost similar to OPC mortar and at ages closer to 91 days. Whereas, compressive strength of fly ash mortar is higher than OPC, showing higher reactivity of fly ash at early ages.

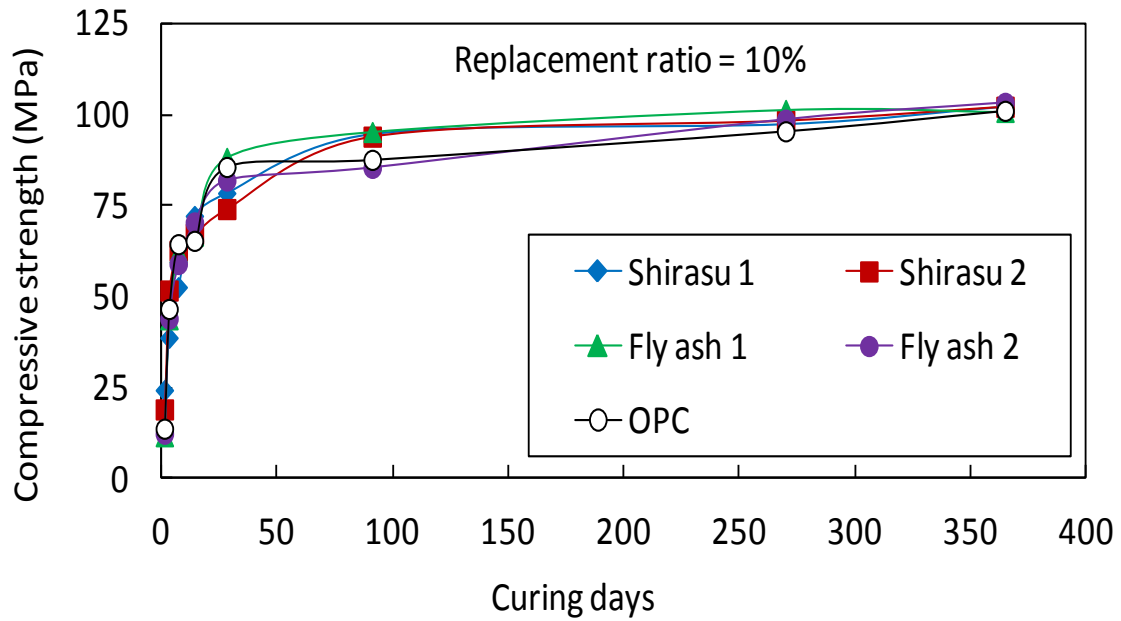


Fig. 3.3 Compressive strengths of all mortars with material age for W/B=40% with replacement ratio of 10%

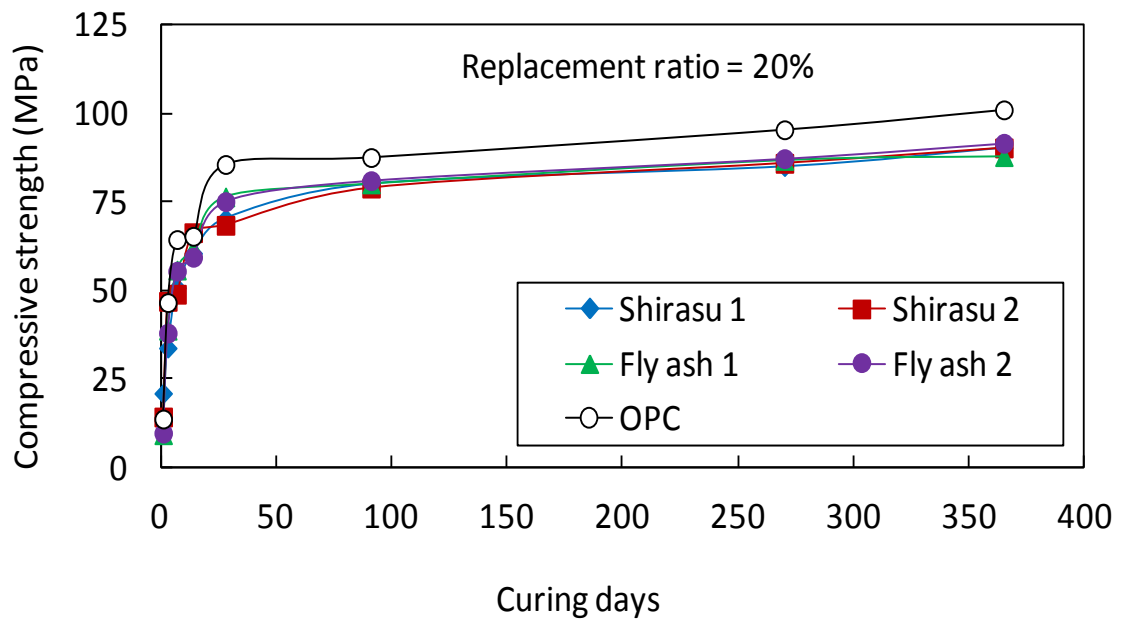


Fig. 3.4 Compressive strengths of all mortars with material age for W/B=40% with replacement ratio of 20%

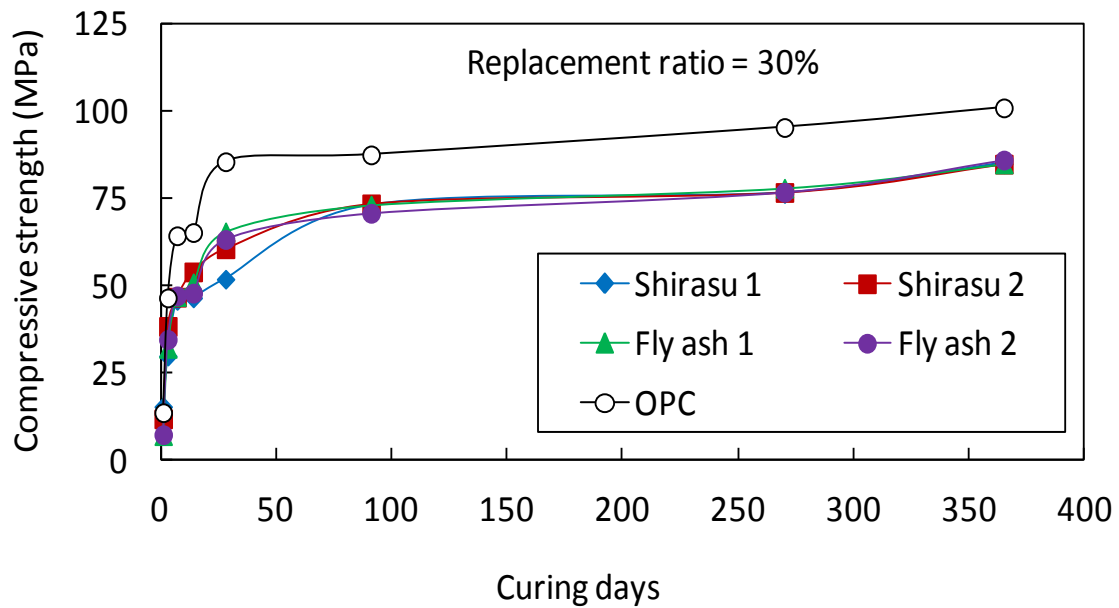


Fig. 3.5 Compressive strengths of all mortars with material age for W/B=40% with replacement ratio of 30%

Between 28 days and 91 days of curing, the rate of hydration of OPC has maintained the reactivity. Shirasu starts hydrating gradually after a longer duration of curing. Beyond 91 days, both OPC and Shirasu mortars exhibited improvement in compressive strength up to one year. Shirasu mortars perform as well as OPC mortar. At this stage of curing, OPC hydration may have ceased and pozzolanic reaction of Shirasu may have initiated efficiently. High early strength gain of OPC due to cement hydration has been demonstrated by the higher strength at early ages as compared to pozzolanic binders. Also, as the replacement ratio of Shirasu increases, the compressive strength becomes much lesser compared to OPC after 1 year curing. But, Shirasu mortars beyond 270 days of curing have exhibited pozzolanic reactivity of Shirasu and have matched compressive strength gained on fly ash mortar. For all replacement ratios, compressive strength of Shirasu mortars is equal to fly ash mortars after 1 year of curing. Especially,

for Shirasu and fly ash replacement ratio of 10%, the compressive strength of Shirasu and fly ash mortars are equal to OPC. These observations confirm long term pozzolanic reaction of Shirasu.

The bending strength of all mortars for W/B=40% are shown in Fig. 3.6, Fig. 3.7 and Fig. 3.8 with different replacement ratios. Similar to the case of compressive strength in Fig. 3.3, Fig. 3.4 and Fig. 3.5, the bending strength of fly ash mortars are higher at early ages (around 3 months) than the Shirasu mortars. At longer duration of curing, i.e. around 270 days up to 1 year, bending strength of Shirasu mortars is almost same compared to the fly ash mortars. This confirms the long term pozzolanic reaction of Shirasu. Also, difference in bending strength of mortar with increase in replacement ratio after 1 year curing is lesser than in the case of compressive strength.

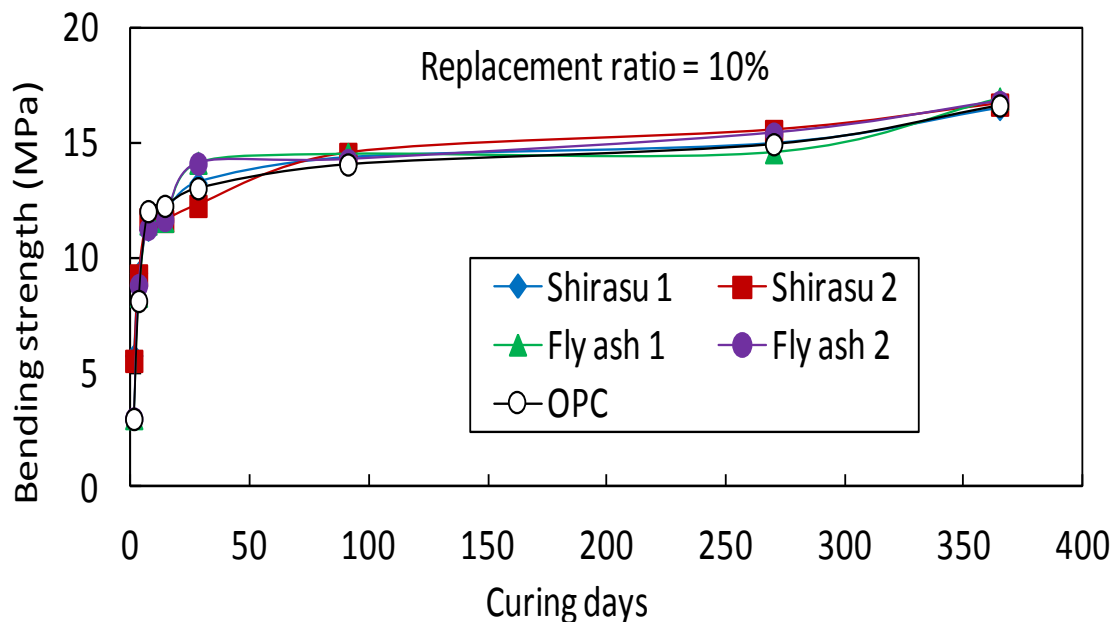


Fig. 3.6 Bending strengths of all mortars with material age for W/B=40% with replacement ratio of 10%

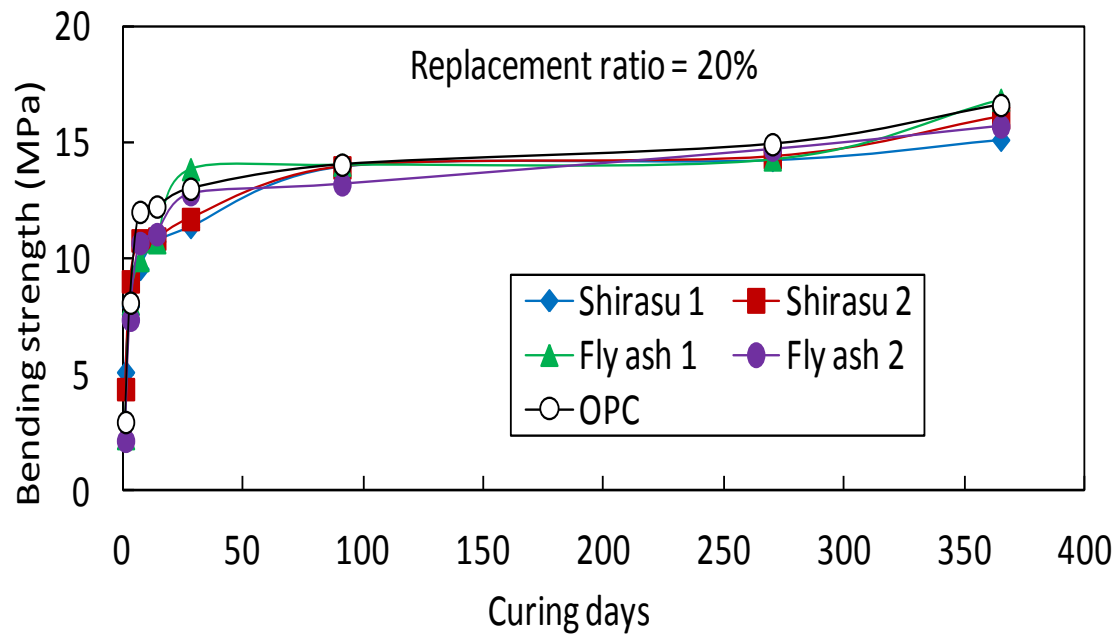


Fig. 3.7 Bending strengths of all mortars with material age for W/B=40% with replacement ratio of 20%

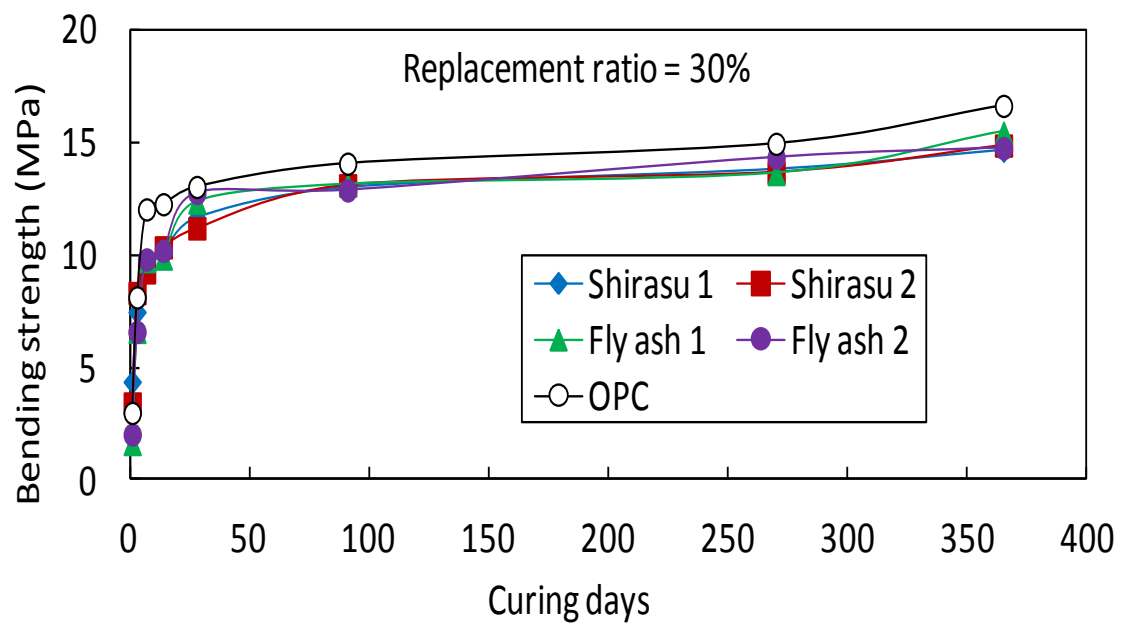


Fig. 3.8 Bending strengths of all mortars with material age for W/B=40% with replacement ratio of 30%

But, similar to compressive strength, bending strength for all mortars with replacement ratio of 10% is equal to OPC after 1 year curing.

#### **Strength of mortars with material age for W/B=50%**

The compressive strength of mortars with W/B=50% (illustrated in Fig. 3.9, Fig. 3.10 and Fig. 3.11) are comparatively lesser compared to mortar with W/B=40% which complies with the theoretical observations from past researches. Even though such a case arises, for replacement ratio of 10%, the compressive strength of all mortars is almost same. As the replacement ratio increases, there is decrease in the compressive strength. Particularly, at early stages of curing, the difference between compressive strength of Shirasu and fly ash mortars is higher compared to W/B=40%. However, at longer curing periods the difference in compressive strength reduces. This effect is due to the pozzolanic reactions of Shirasu at later stages of curing.

The compressive strength of Shirasu mortars does not increase much between curing periods of 28 days to 270 days. At this stage, cement hydration may have completed. Hence the compressive strength between 28 days to 270 days can be attributed to cement hydration. But at curing periods between 270 days and 1 year, increase in compressive strength is observed for Shirasu mortars. This is due to the long term pozzolanic reaction of Shirasu by reacting with calcium hydroxide produced after completion of cement hydration at longer material ages.

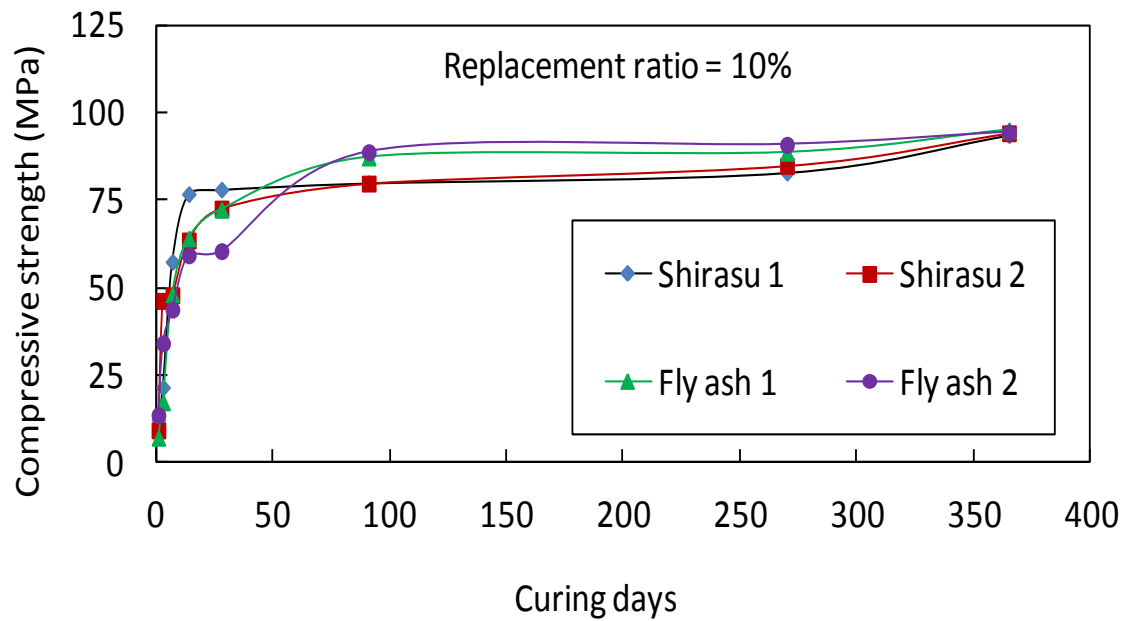


Fig. 3.9 Compressive strengths of all mortars with material age for W/B=50% with replacement ratio of 10%

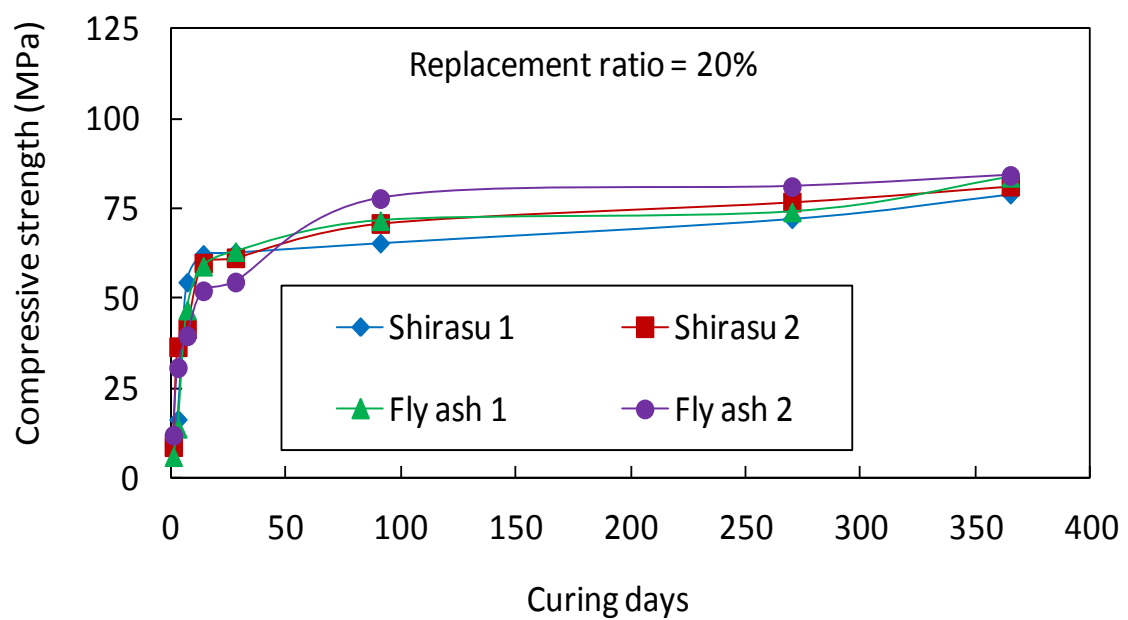


Fig. 3.10 Compressive strengths of all mortars with material age for W/B=50% with replacement ratio of 20%

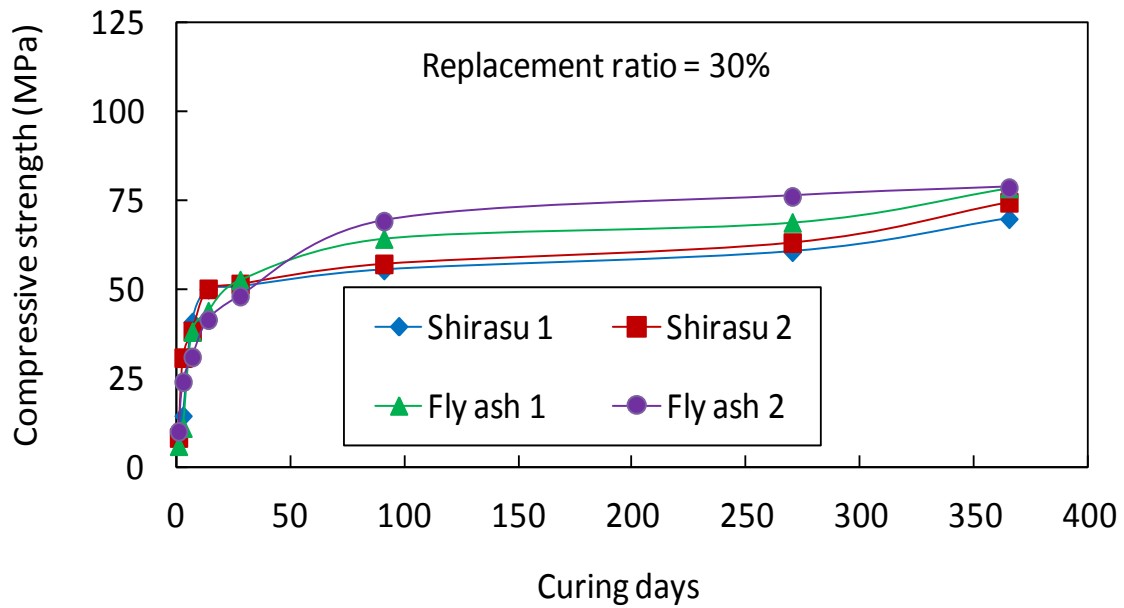


Fig. 3.11 Compressive strengths of all mortars with material age for W/B=50% with replacement ratio of 30%

The bending strength results of all mortars for W/B=50% are illustrated in Fig. 3.12, Fig. 3.13 and Fig. 3.14. As in the case of compressive strength results, the differences in bending strength between Shirasu and fly ash minimize at longer duration of curing period. At early ages of curing the fly ash mortars have higher flexural strength compared to Shirasu mortars. But, at longer durations of curing, the difference between the flexural strength of fly ash and Shirasu is very less. However, the difference in bending strength is larger in W/B=50% when compared to W/B=40%. This is the effect of higher water to binder ratio, where, amount of binder reduces resulting in relatively lesser amount of cement. It is observed that maximum flexural strength is obtained for replacement ratio of 10% and decreases as the replacement ratio increases. Regardless of W/B, the bending strength of Shirasu mortar with Shirasu replacement of 10% is almost equal to fly ash.



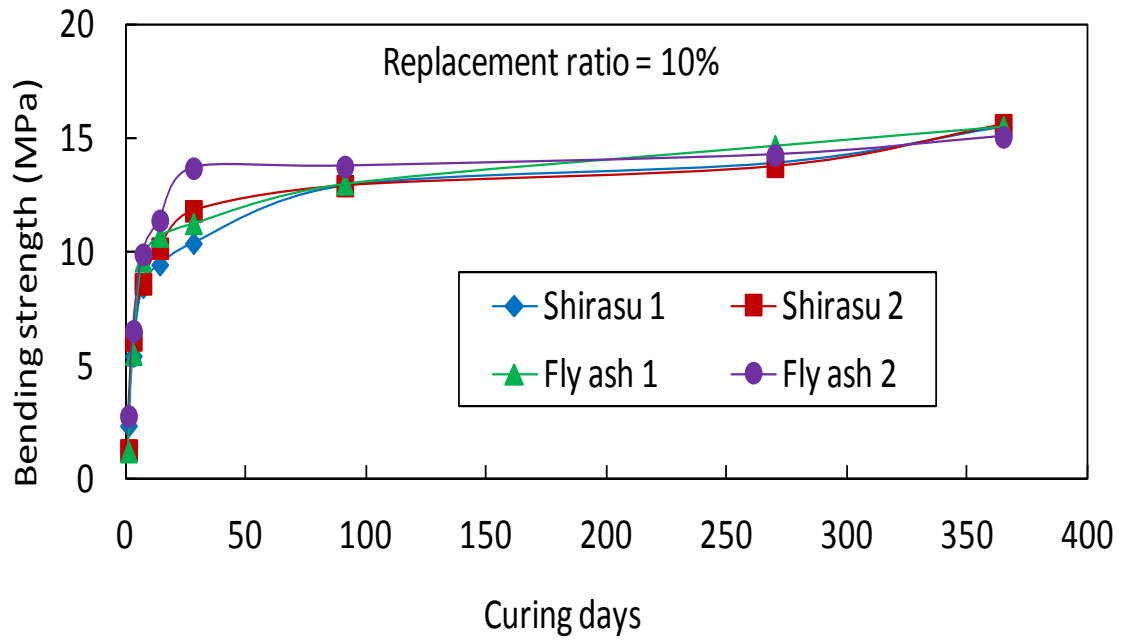


Fig. 3.12 Bending strengths of all mortars versus age for W/B=50% with replacement ratio of 10%

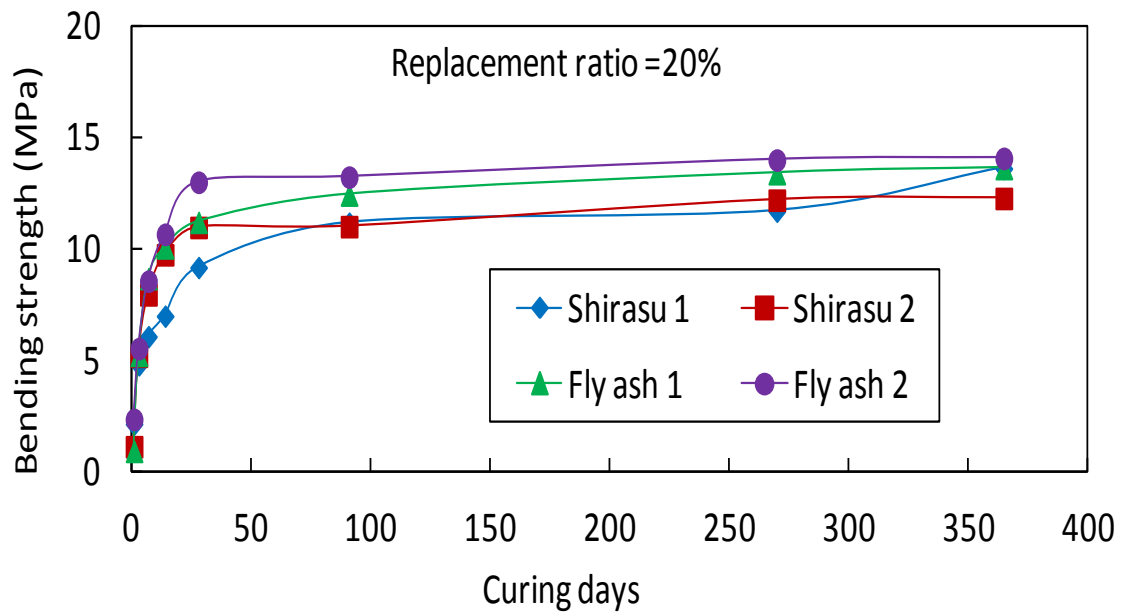


Fig. 3.13 Bending strengths of all mortars versus age for W/B=50% with replacement ratio of 20%

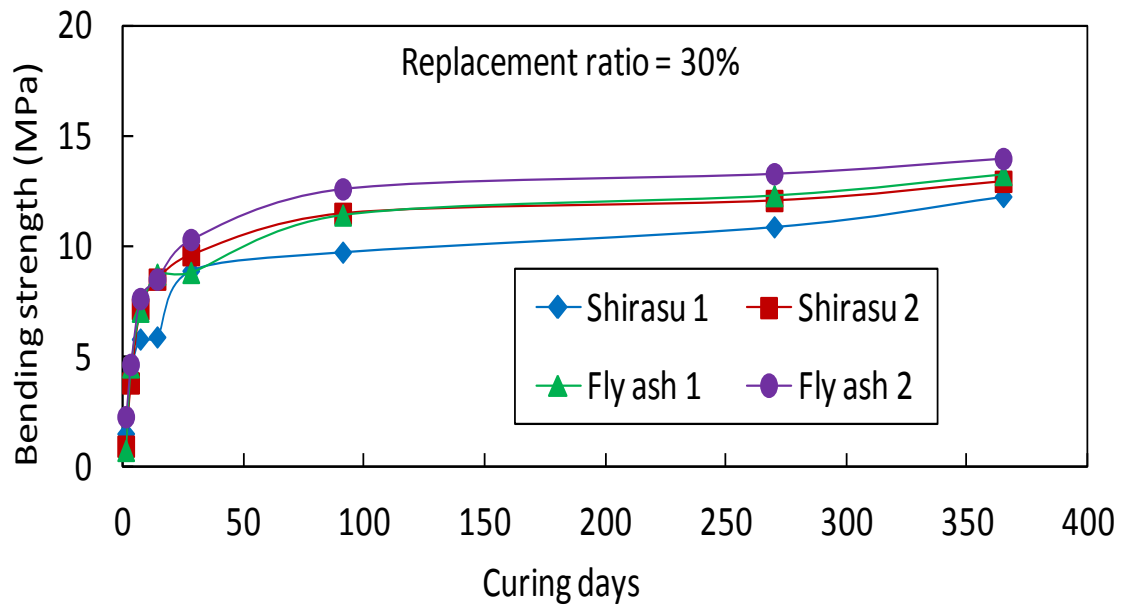


Fig. 3.14 Bending strengths of all mortars with material age for W/B=50% with replacement ratio of 30%

#### Strength of mortars with material age for W/B=60%

The compressive strength of mortars with W/B=60% have comparatively lesser strength compared to mortars with W/B=40% and W/B=50% as illustrated in Fig. 3.15, Fig. 3.16 and Fig. 3.17. Compressive strength of fly ash mortars are higher than Shirasu mortars and the difference seems to be larger compared to W/B=40% and 50% at all ages. As the water binder ratio increases, absolute amount of binder in the mix reduces. Hence, lesser amount of calcium hydroxide produced due to lesser cement content. Therefore, increase in replacement ratio for higher water binder ratio reduces the compressive strength drastically. The compressive strength of Shirasu mortar with replacement ratios of 10% and 20% are similar at longer material ages confirming long term pozzolanic reaction.

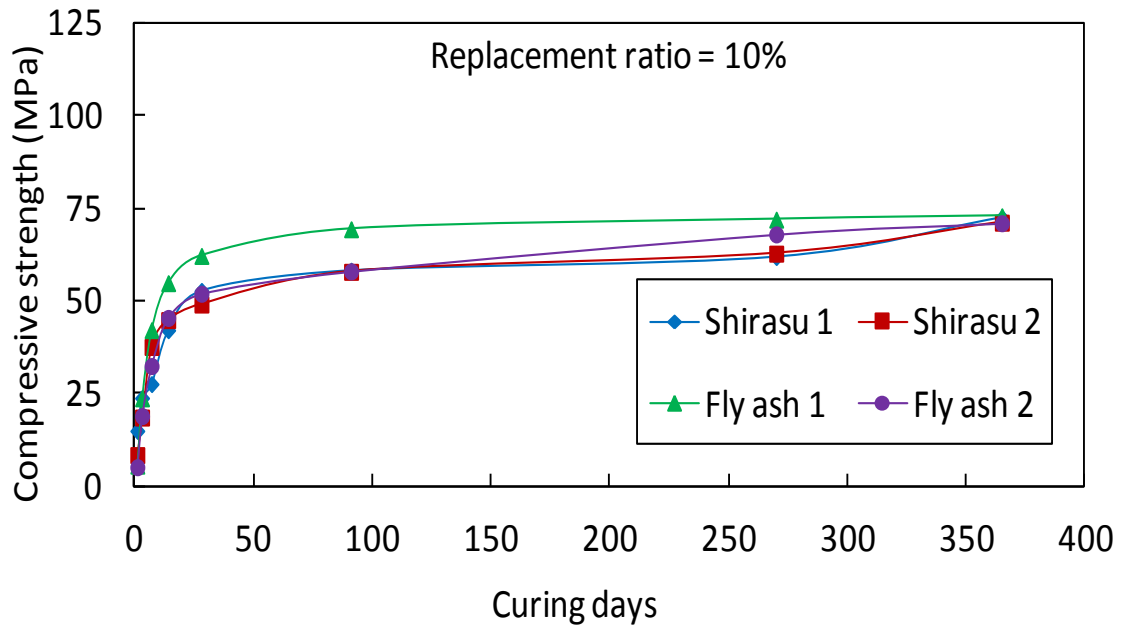


Fig. 3.15 Compressive strengths of all mortars with material age for W/B=60% with replacement ratio of 10%

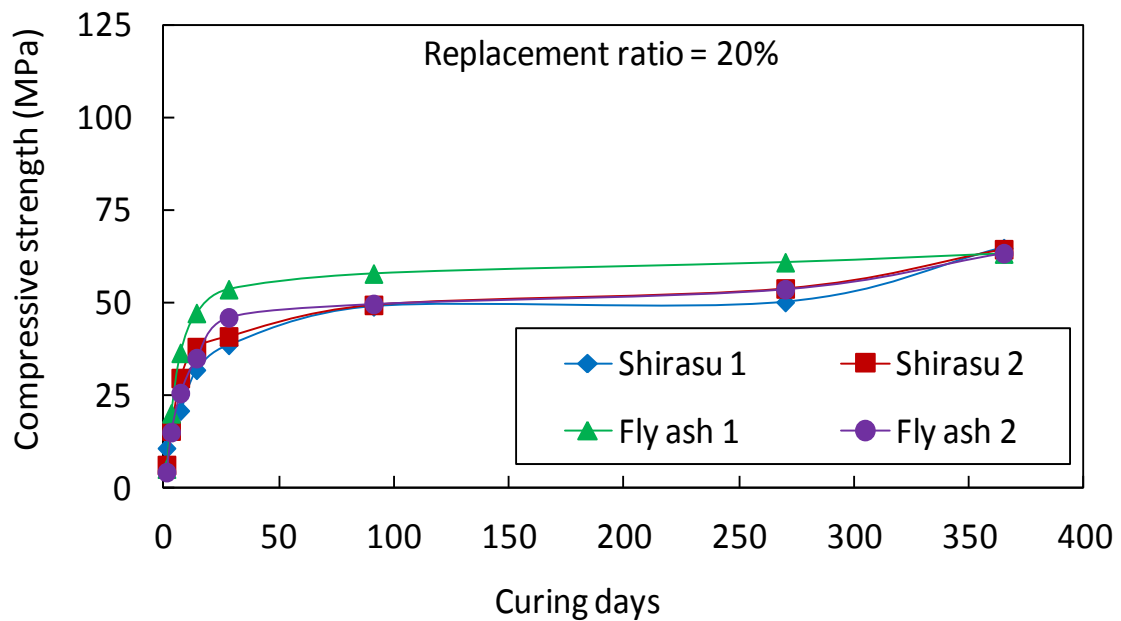


Fig. 3.16 Compressive strengths of all mortars with material age for W/B=60% with replacement ratio of 20%

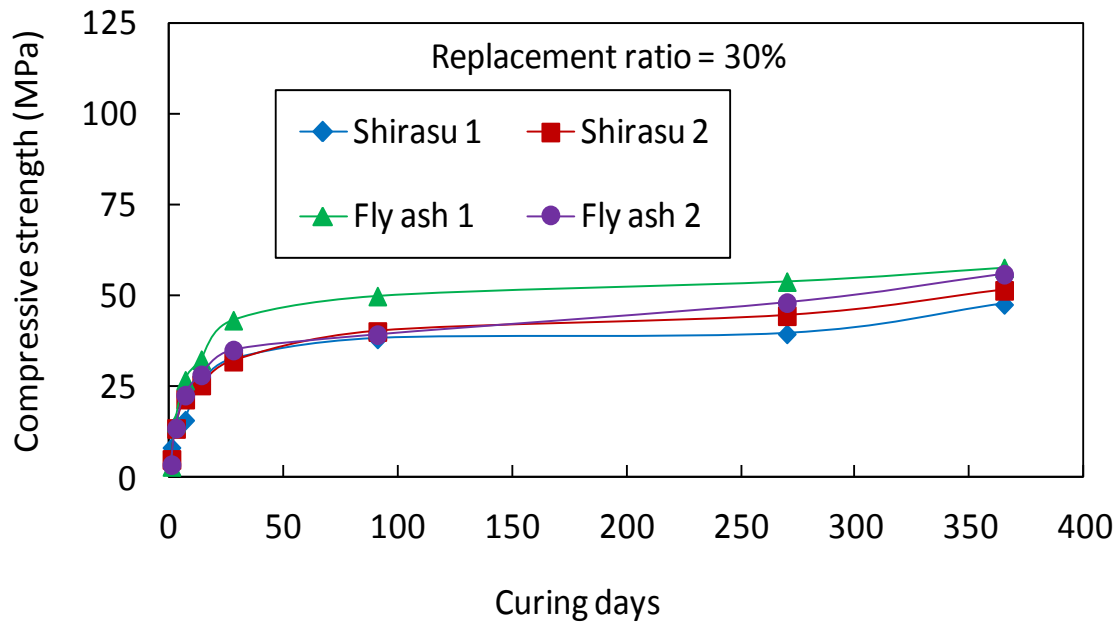


Fig. 3.17 Compressive strengths of all mortars with material age for W/B=60% with replacement ratio of 30%

Similar to W/B=50%, the compressive strength of mortars with W/B=60% do not increase between curing periods of 28 days and 270 days. But at later stages of curing (beyond 270 days) increase in the compressive strength of Shirasu mortar is observed up to 1 year. The strength is expected to increase beyond 1 year curing period.

The Bending strength of all mortars with W/B=60% for different replacement levels are shown in Fig. 3.18, Fig. 3.19 and Fig. 3.20. The flexural strength of Shirasu mortars are clearly less compared to fly ash at early ages of curing. But the difference is lesser compared to W/B=50%. The bending strength of Shirasu mortars at longer ages of curing are observed to be almost equal to bending strength of fly ash mortars.

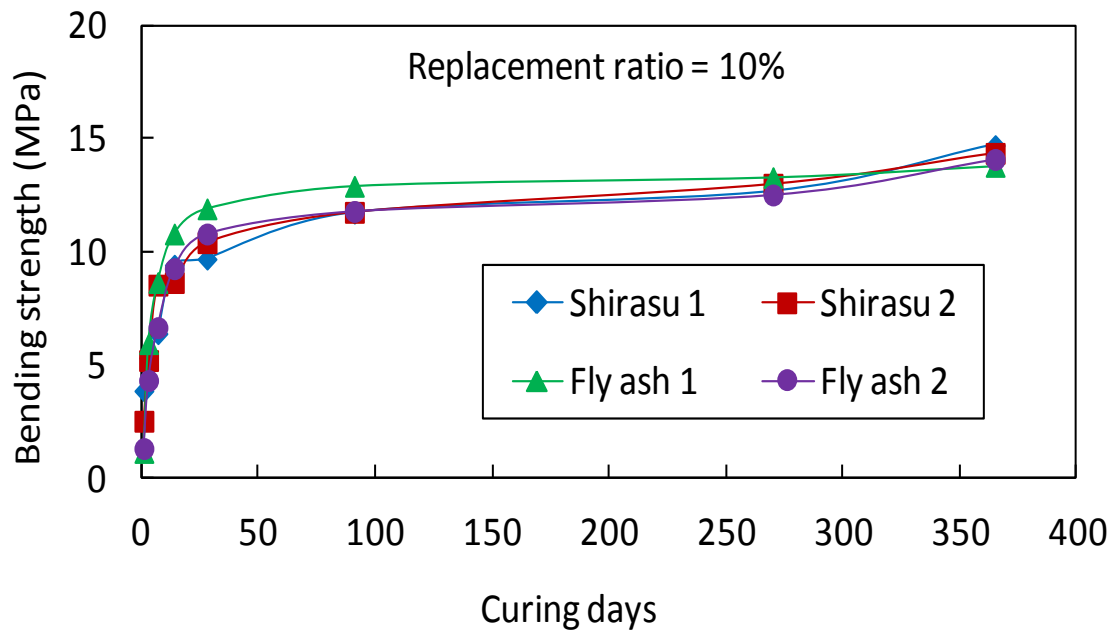


Fig. 3.18 Bending strengths of all mortars with material age for W/B=60% with replacement ratio of 10%

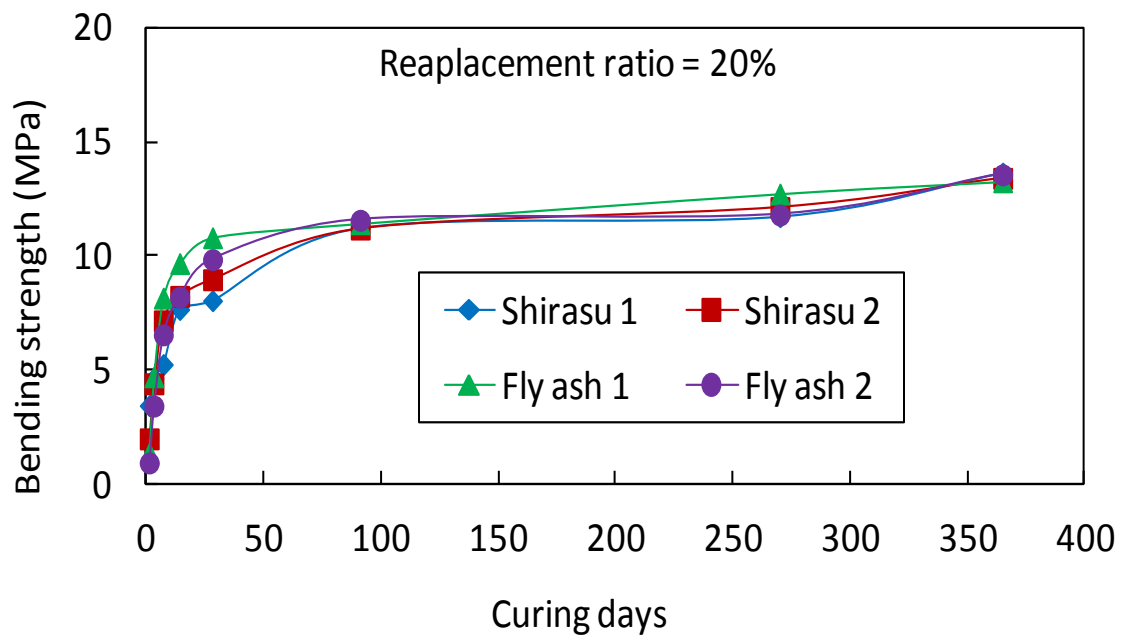


Fig. 3.19 Bending strengths of all mortars with material age for W/B=60% with replacement ratio of 20%

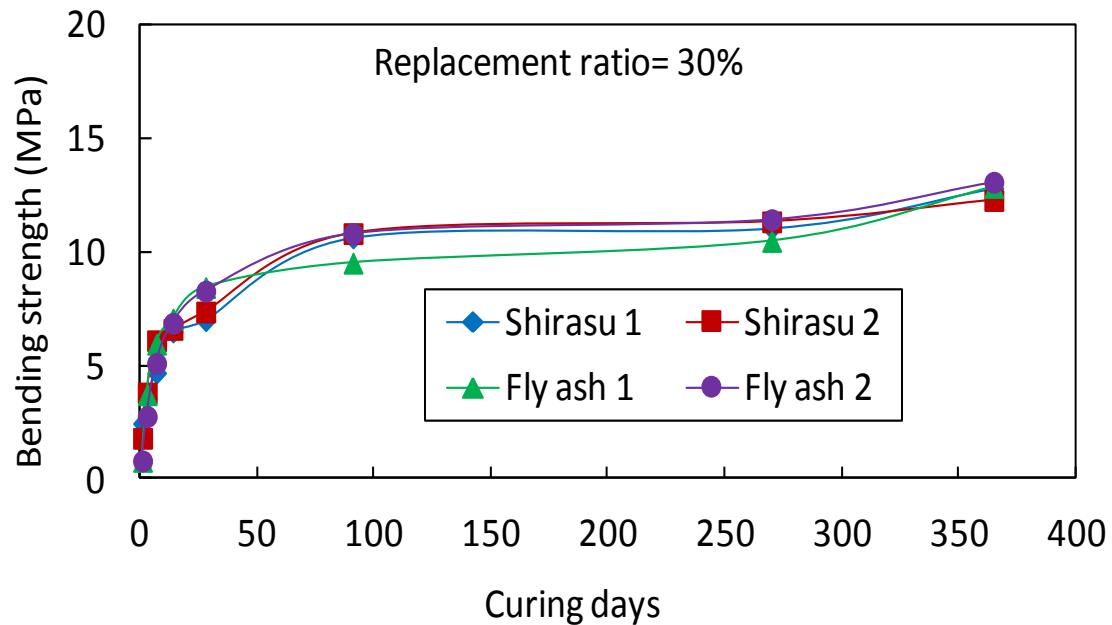


Fig. 3.20 Bending strengths of all mortars with material age for W/B=60% with replacement ratio of 30%

### Effect of water to binder ratio and replacement ratio on strength development

Compressive strength comparison between Shirasu and fly ash mortars are done for different curing periods as shown in Fig. 3.21, Fig. 3.22 and Fig. 3.23. In the case of 28 days of curing period, overall compressive strength of fly ash mortars are higher than Shirasu mortars. As fly ash particles are spherical and have smooth surface, the ball bearing effect on the fresh concrete increases the workability and compaction ability. The property of fresh concrete in the case of fly ash is much better than other pozzolans because of its particle nature. Fly ash also reduces the demand of water for mixing in concrete for the same workability. Hence, the early age strength of fly ash proves to be much better. Shirasu particles on the other hand are irregular in shape and highly porous as they are pyroclastic flow deposit.

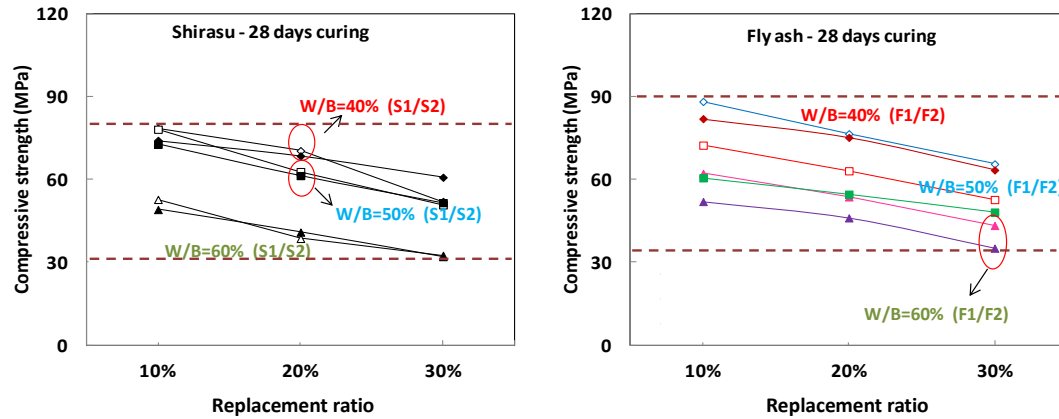


Fig. 3.21 Compressive strength versus replacement ratio of Shirasu and fly ash mortars for 28 days curing

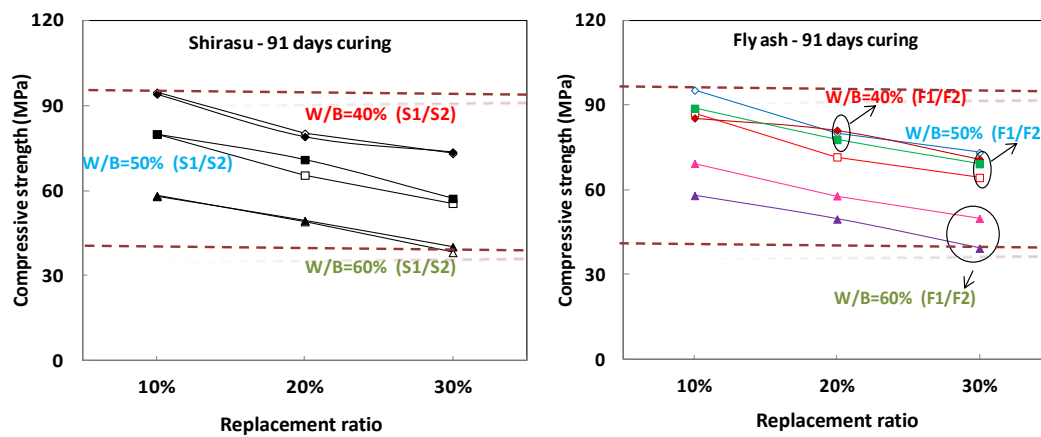


Fig. 3.22 Compressive strength versus replacement ratio of Shirasu and fly ash mortars for 91 days curing

Workability of concrete in some W/B is much low when compared to fly ash and demands more water for the same workability. Workability can also be improved by introduction of plasticizers or other admixtures. Hence the early age strength of Shirasu mortars is lower. The difference in compressive strength between fly ash Shirasu mortar decreases at a curing period of 91 days as illustrated in the figure. Especially after 1 year curing, there is no difference in strength between Shirasu and fly ash.

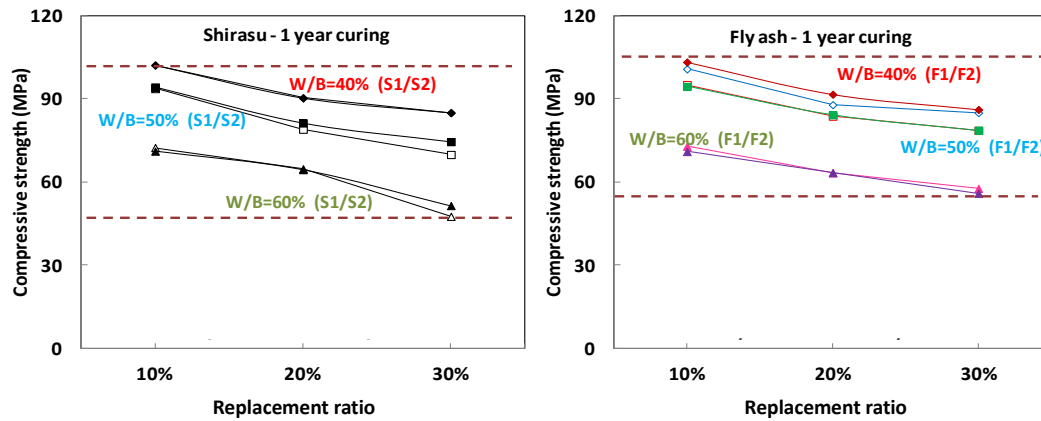


Fig. 3.23 Compressive strength versus replacement ratio of Shirasu and fly ash mortars for 1 year curing

The compressive strength of Shirasu mortar is equal to fly ash mortar in the long term. The rate of pozzolanic reaction of Shirasu is low at early stages, but increases significantly to match with the fly ash. Even though the early stage pozzolanic reactivity of Shirasu is considered to be slow, the long term strength of Shirasu mortar is almost equal to that of fly ash mortar. It is clearly evident that compressive strength of mortar with 10% replacement level of Shirasu as binder with water binder ratio of 40% is the optimum. For higher percentages of replacement and water binder ratio, decrease in strength is indicated. Even though there is a decrease in strength of mortar as the replacement increases, there is a certain trend in the result which indicates that the Shirasu is reacting, but at a slower rate for higher replacement ratios. This is because of relatively lesser content of cement which reduces the absolute amount of calcium hydroxide necessary for pozzolanic reaction of Shirasu at later stages. Relatively lesser content of cement with higher Shirasu content needs longer curing periods for pozzolanic reaction to affect the strength development of mortars.



### Ratio of compressive strength of Shirasu mortar to the fly ash mortar

The compressive strength of Shirasu mortar in the long term is confirmed to be almost equal to the compressive strength of fly ash. But, the rate of strength gain or reactivity of Shirasu when compared to fly ash is not easily understood from the previous results on compressive strength and bending strength. For this reason, the ratio of compressive strength of Shirasu mortar to the compressive strength of fly ash mortar (“S/F”) is calculated to estimate the reactivity of Shirasu. The comparison of S/F with age for different W/B and replacement ratios are illustrated in Fig. 3.24, Fig. 3.25 and Fig. 3.26. For all cases of W/B and replacement ratios, the S/F is lesser than 1 for 28 days curing. As the curing period increases the S/F increases in the case of mortars with W/B=40% and 60%. S/F is almost equal to 1 in case of replacement ratios of 10% and 20% for all W/B at 1 year curing period. This confirms the long term pozzolanic reactivity of Shirasu.

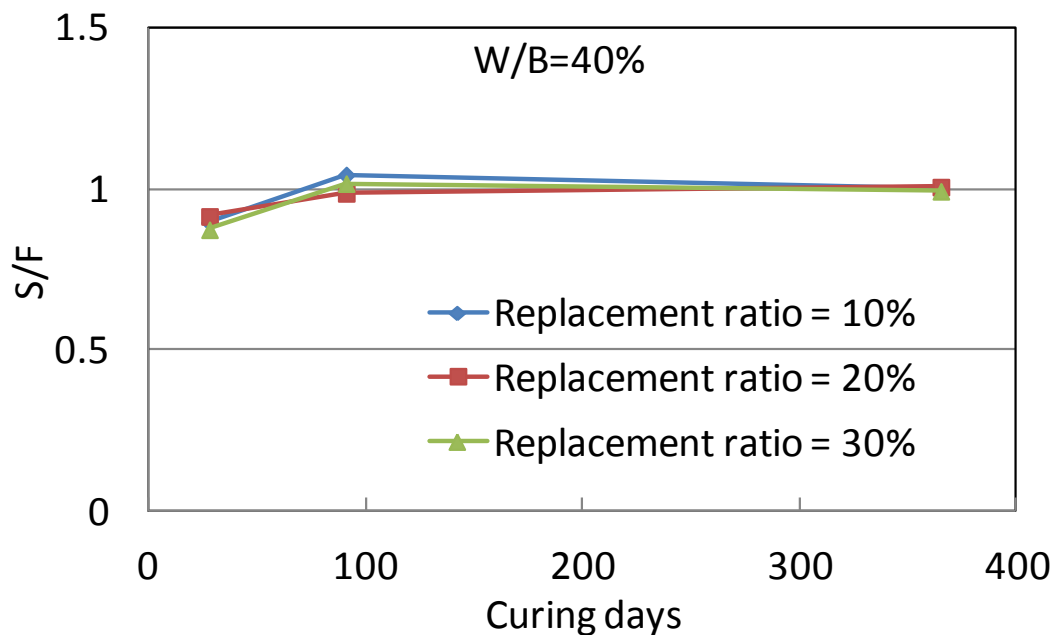


Fig. 3.24 S/F for W/B=40% with different replacement ratios

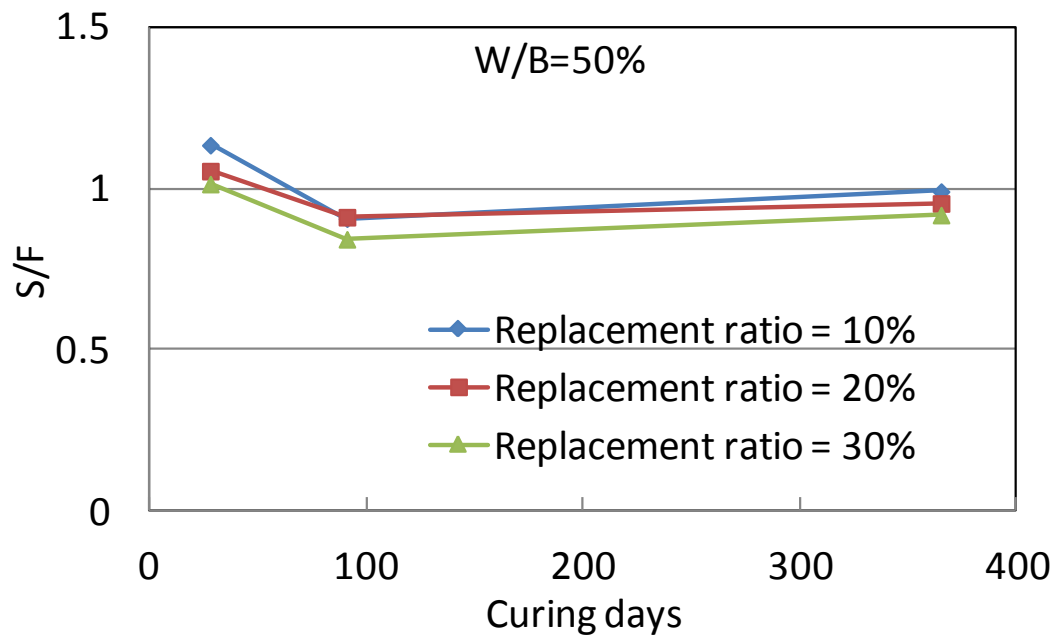


Fig. 3.25 S/F for W/B=50% with different replacement ratios

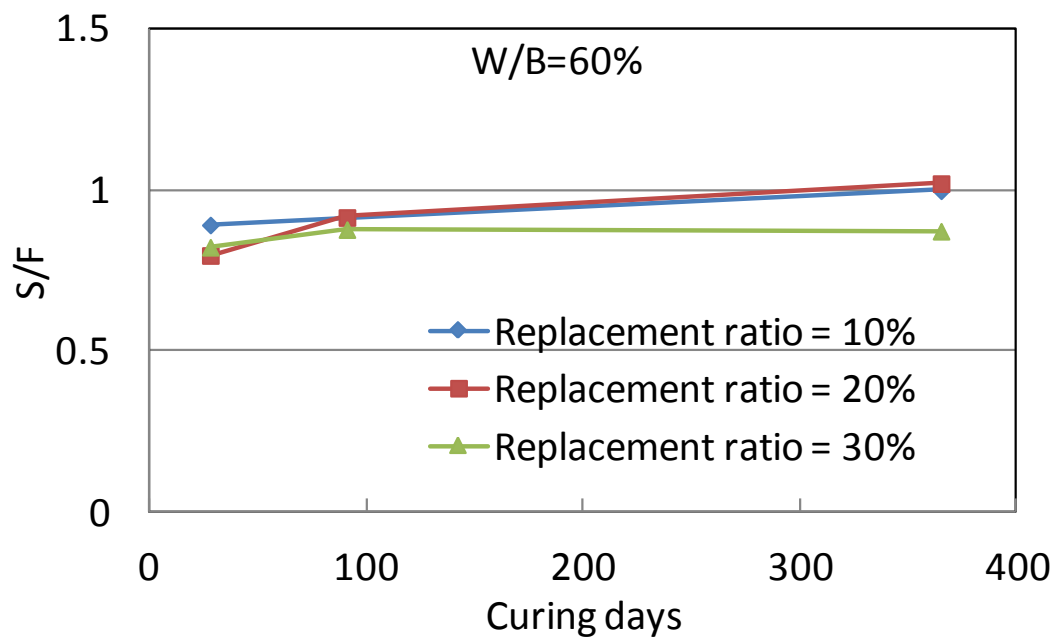


Fig. 3.26 S/F for W/B=60% with different replacement ratios

### Strength of Shirasu mortars with mix proportion considering water absorption

High porous nature of Shirasu particle increases the water absorption characteristics. This seems to change the actual water binder ratio. For this reason, Shirasu mortars with the mix proportion altered with increase in water content are also prepared. Fig. 3.27 and Fig. 3.28 show the comparison of compressive strength and bending strength of Shirasu mortars with mix proportion considering water absorption (altered) with those of mix proportion without considering water absorption (original). Here Shirasu 1, Shirasu 2, Fly ash 1, Fly ash 2 are mix proportions of mortar without considering water absorption with two types of Shirasu and two types of fly ash respectively and Shirasu 1\* and Shirasu 2\* are mortars with mix proportions considering water absorption for two types of Shirasu.

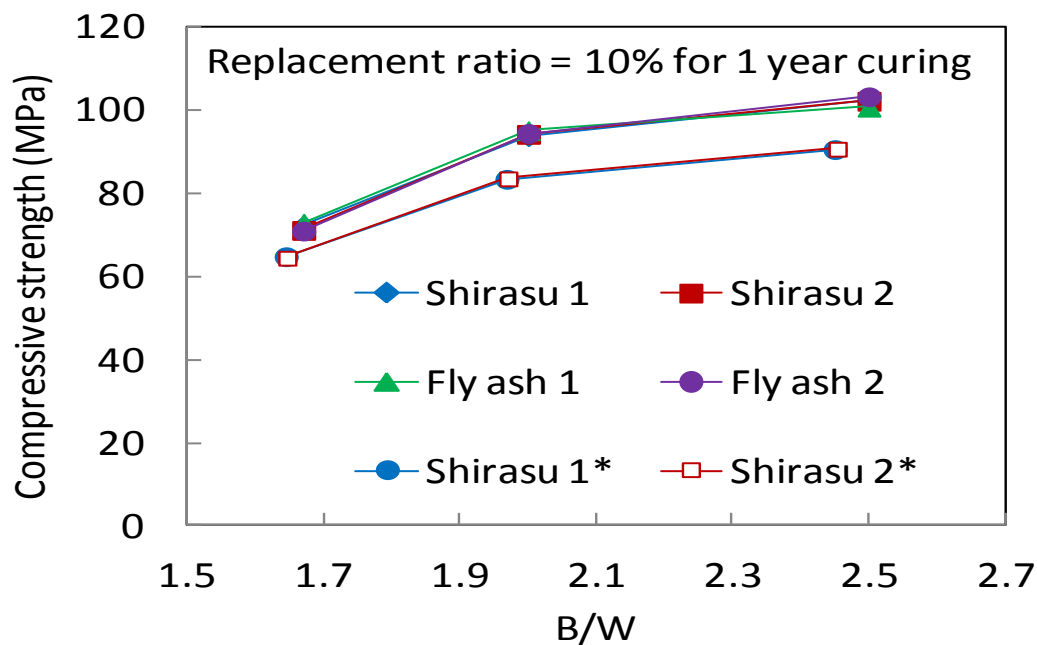


Fig. 3.27 Compressive strength comparison of Shirasu mortar between original mix proportions of and altered mix proportions

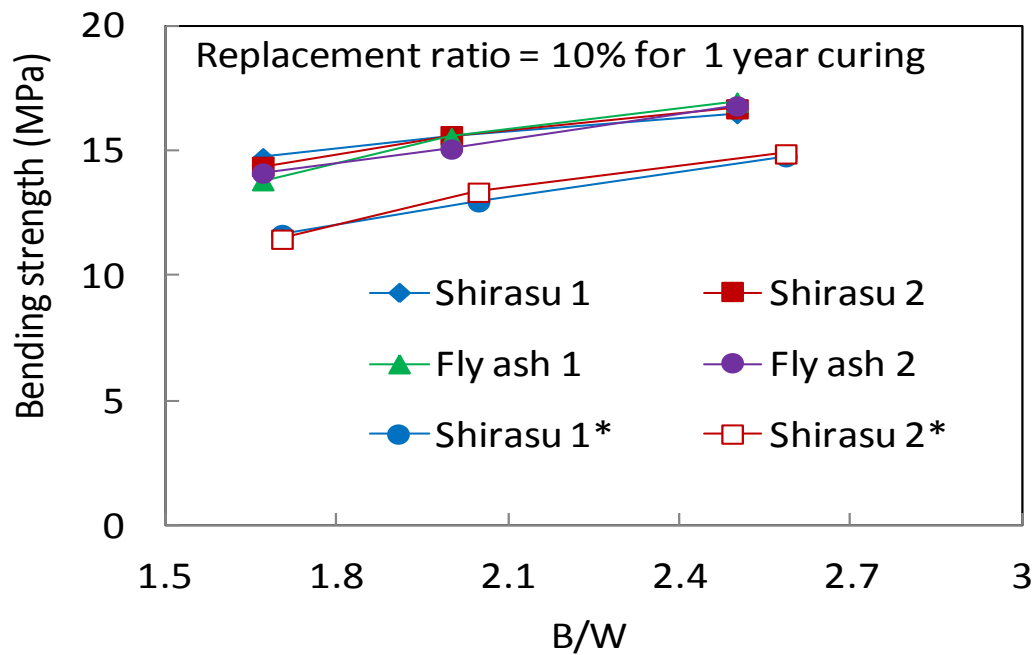


Fig. 3.28 Bending strength comparison of Shirasu mortar between original mix proportions of and altered mix proportions

Super plasticizers have been used for certain mix proportions for water binder ratio of 40% to match the flow characteristics of mortar with the other mix proportions. The graphs indicate the comparison of strength versus binder-water ratio (“B/W”). It is obvious that the water binder ratio for altered Shirasu mortar mix proportion is higher than the original mix proportion and hence the bending strengths and compressive strengths of altered Shirasu are lowered slightly. However, the comparative trends are similar and the strengths of altered mix proportions are almost similar to the original Shirasu mortar at 365 days curing period.

The difference in compressive strength between Shirasu mortar with mix proportion considering water absorption and mix proportion without considering water absorption

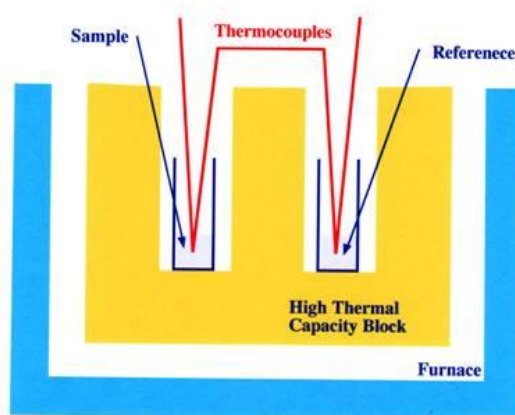
are less. This is attributed to the fact that fine particles of Shirasu are used as cement replacement material. Even if the water absorption of Shirasu is high, fine particles have relatively lesser water absorption property. Shirasu, if used as fine aggregate may affect the actual water binder ratio designed for casting. As fine Shirasu particles are used, it does not affect water content in the mix at such high magnitudes. The original Shirasu mortars with W/B=40% has a lower flow characteristics for all levels of replacements. The alterations in mix proportion of Shirasu mortar to compensate for the water absorption capacity improved the flow characteristics.

## Differential Thermal Analysis (DTA)

Differential thermal analysis (or DTA) is a thermo-analytic technique where the material under study and an inert reference are made to undergo identical thermal cycles, while recording any temperature difference between sample and reference. This differential temperature is then plotted against time, or against temperature (DTA curve or thermogram). Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference.



Picture 1 DTA machine



Picture 2 Principle of differential thermal analysis

A DTA consists of a sample holder comprising thermocouples, sample containers and a ceramic or metallic block (Picture 1); a furnace; a temperature programmer; and a recording system. The key feature is the existence of two thermocouples connected to a voltmeter. One thermocouple is placed in an inert material ( $\text{Al}_2\text{O}_3$ ), while the other is placed in a sample of the material under study (Picture 2). As the temperature is increased, there will be a brief deflection of the voltmeter if the sample is undergoing a phase transition. This occurs because the input of heat will raise the temperature of the inert substance, but be incorporated as latent heat in the material changing phase.

The rate of consumption of calcium hydroxide by Shirasu in pozzolanic reaction is not clearly understood. For this purpose Shirasu and Calcium hydroxide (CH) paste is made. Two different sizes of Shirasu are used,  $75\mu\text{m}$  and  $150\mu\text{m}$  for DTA analysis. Shirasu and Calcium hydroxide are mixed in water according to the mix proportion shown in Table 3.5. The specimens are cured and the powdered samples are taken from these specimens for DTA analysis at different curing periods. In DTA, sample is heated up to  $1000^\circ\text{C}$ . At a particular temperature ( $400^\circ\text{C}$  to  $600^\circ\text{C}$ ), components of calcium hydroxide in the sample gets dehydrated. The mass of calcium hydroxide can be analyzed by Thermo-gravimetric Analysis (TGA) which measures the mass change of a material as a function of temperature and time, in a controlled atmosphere. Mass change between temperatures of  $400^\circ\text{C}$  to  $600^\circ\text{C}$  is recorded by the machine which is connected to a PC for further analysis using software. In this experimental study, only Shirasu and calcium hydroxide powder are used to make paste to simulate the condition of long term pozzolanic reaction of Shirasu after cement hydration. . As no cement is used, calcium hydroxide is readily available for Shirasu to undergo pozzolanic reaction. This will

increase the rate of pozzolanic reactivity of Shirasu unlike mortar, where pozzolanic reaction of Shirasu starts after longer periods depending on the degree of cement hydration and calcium hydroxide availability.

Table 3.5 Shirasu paste with calcium hydroxide (unit weight, kg/m<sup>3</sup>)

W/B	Shirasu/Binder	Water	Shirasu	Calcium Hydroxide
60%	50%	582	485	485

The results of DTA analysis for Shirasu particle size under 150µm are shown in Fig. 3.29, Fig. 3.30 and Fig. 3.31 for different set of samples. In these graphs, comparison between different set of samples are done (Sample1, Sample 2 and Sample 3) for each particle size of Shirasu since average of sample do not explain the mechanism clearly. The labels of each trend lines are given at the end of the graphs. From the curves of DTA, the first drop in voltage at 100<sup>0</sup>C shows the water evaporation stage. The second drop in voltage around 400<sup>0</sup>C to 600<sup>0</sup>C is the change of phase (transition) of calcium hydroxide or the dehydration of calcium hydroxide. This is shown as the endotherm in the DTA curve. As seen from the graph, the curve for 28 days has highest drop in voltage at 100<sup>0</sup>C and as the curing period increases the drop in voltage reduces drastically. This means that at early ages of curing of around 28 days, water has not been consumed. Hence the pozzolanic reaction has not yet commenced. This effect can be confirmed by the second stage drop in voltage where the amount of calcium hydroxide is highest for 28 days. As the curing period increases, voltage drop in both the stages decrease.



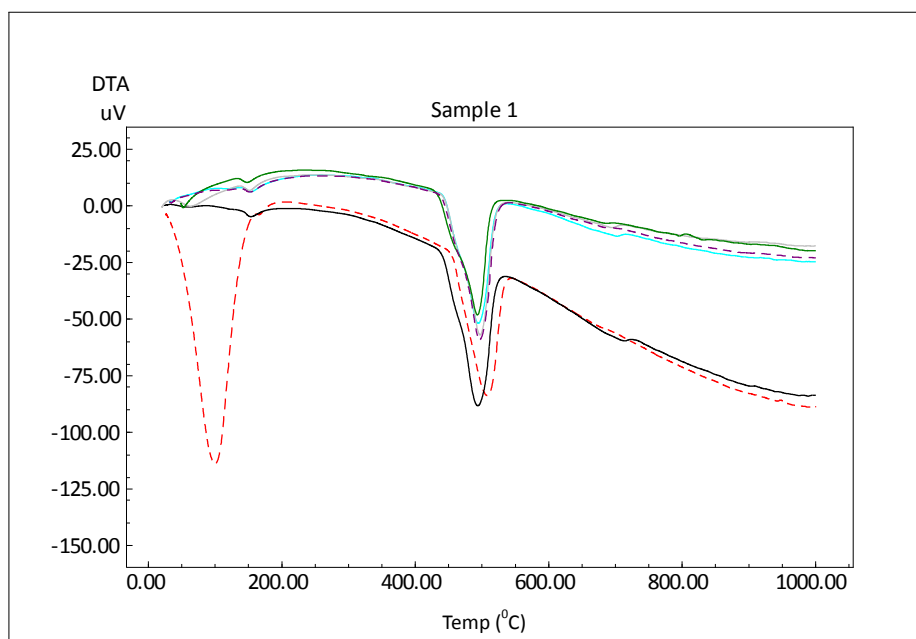


Fig. 3.29 DTA curves of first set of samples for Shirasu particles under 150 $\mu$ m at different curing periods

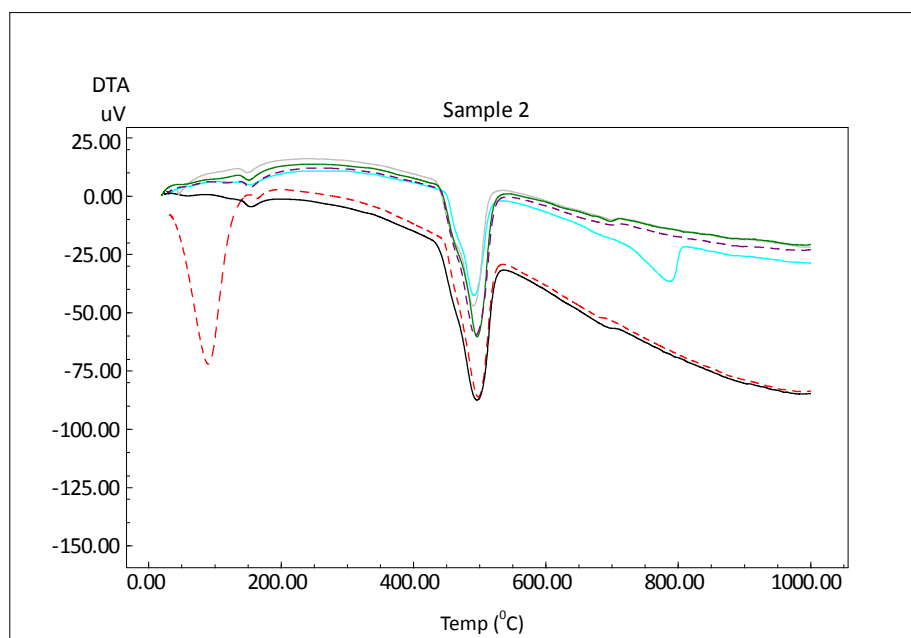


Fig. 3.30 DTA curves of second set of samples for Shirasu particles under 150 $\mu$ m at different curing periods

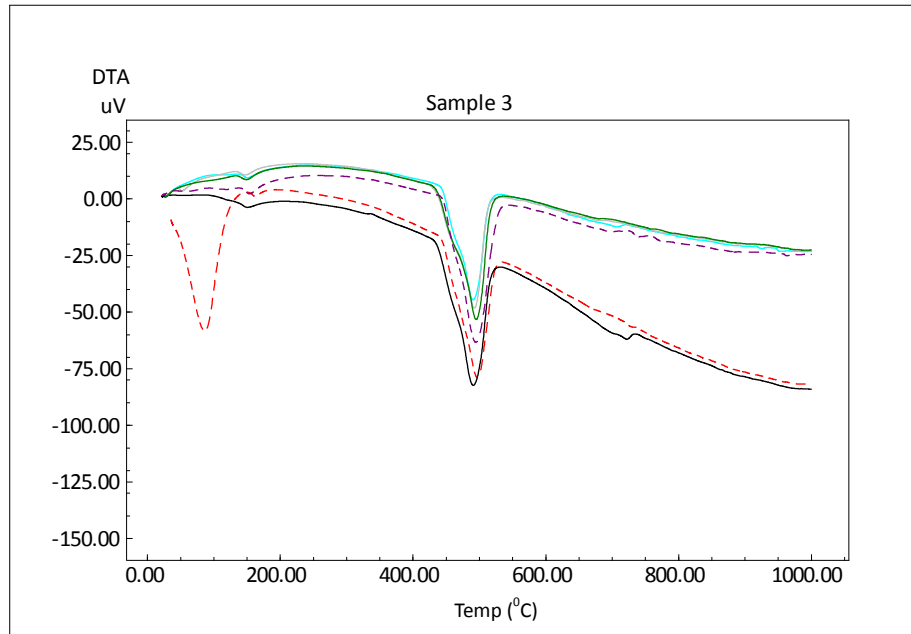


Fig. 3.31 DTA curves of third set of samples for Shirasu particles under 150 $\mu$ m at different curing periods

This is the indication of reduction in evaporation of water (as the water is consumed for pozzolanic reaction) and lesser amount of calcium hydroxide which confirms pozzolanic reaction. The intensity of endothermic peak is highest for 28 days and decreases as the duration of curing increases.

The DTA curves for Shirasu particle size under 75 $\mu$ m are shown in Fig. 3.32, Fig. 3.33 and Fig. 3.34 for different sets of samples. Similar to the DTA curve for Shirasu particles of size under 150 $\mu$ m, the curves have both peaks at around 100 $^{\circ}$ C and 500 $^{\circ}$ C in the case of Shirasu under 75 $\mu$ m. But the first peak is relatively smaller in case of 75 $\mu$ m than 150 $\mu$ m. This may be due to the water absorption capacity of Shirasu. Water absorption increases as the particle size increase because of relative increase in pores.

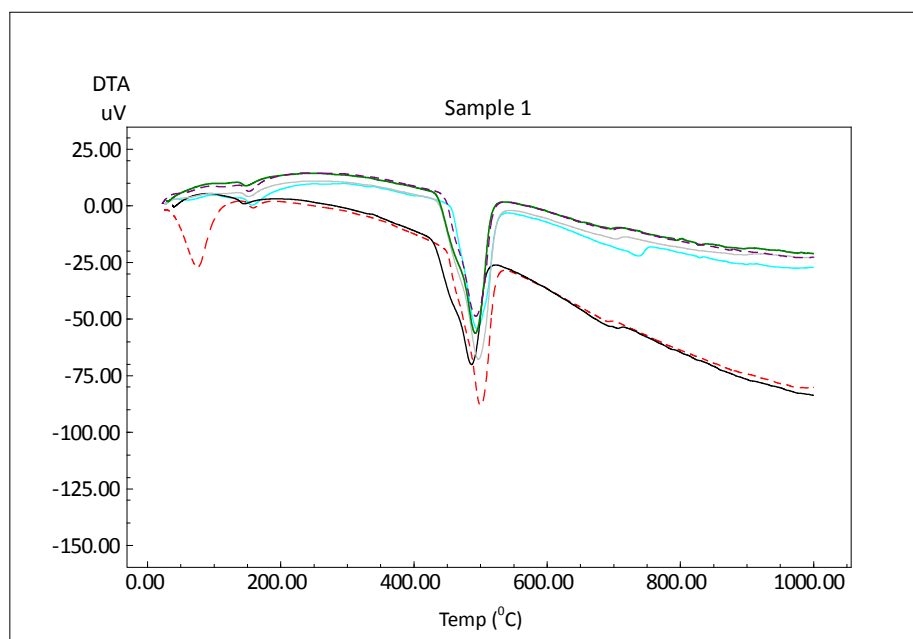


Fig. 3.32 DTA curves of first set of samples for Shirasu particles under 75µm at different curing periods

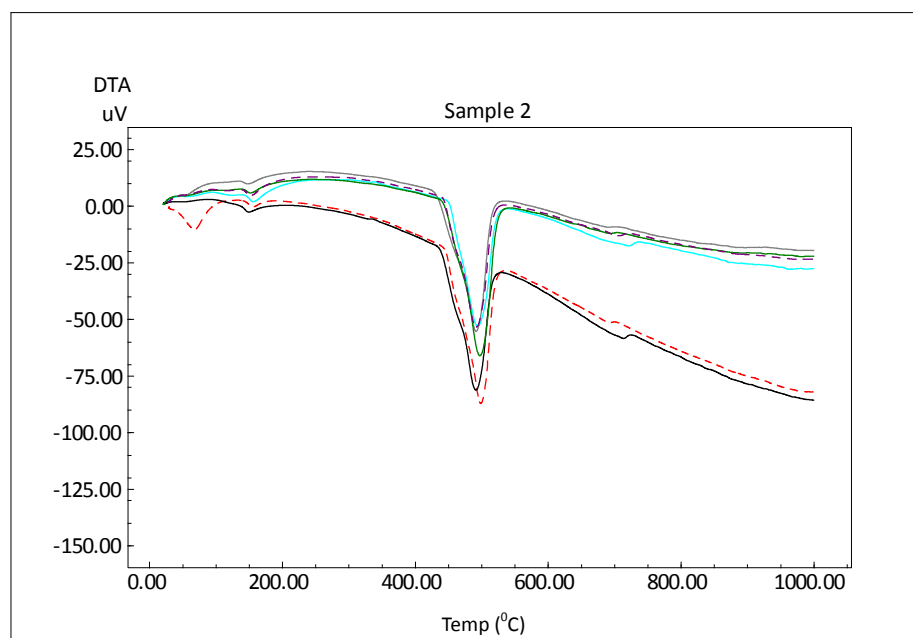


Fig. 3.33 DTA curves of second set of samples for Shirasu particles under 75µm at different curing periods

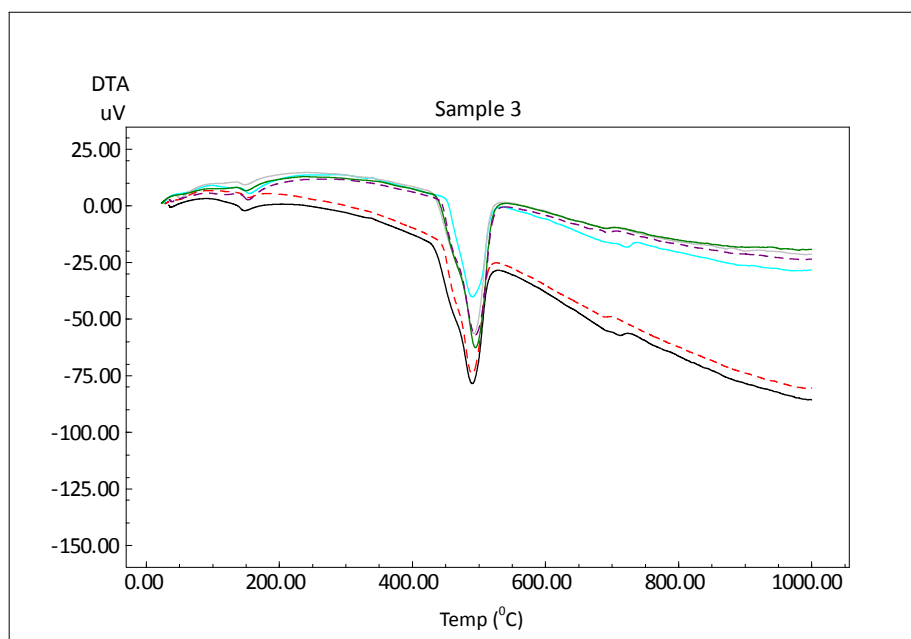
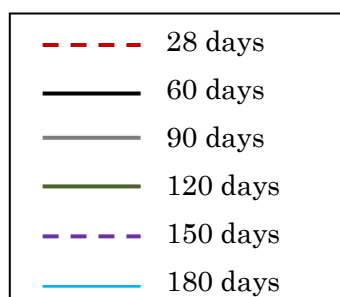


Fig. 3.34 DTA curves of third set of samples for Shirasu particles under 75 $\mu$ m at different curing periods



Voltage drop in both the stages decrease as the curing period increase, which shows lesser evaporation of water (as the water is consumed for pozzolanic reaction) and lesser amount of calcium hydroxide confirming pozzolanic reaction. The intensity of endothermic peak is highest for 28 days and decreases as the duration of curing increases.

Thermo-gravimetric analysis of Shirasu paste for both Shirasu of size under 75 $\mu$ m and

150 $\mu$ m are shown in Fig. 3.35. The calcium hydroxide percentage in samples decreases as the duration of curing increases for both particle sizes of Shirasu. However, the amount of calcium hydroxide is relatively lesser in case of Shirasu of size under 75 $\mu$ m than for 150 $\mu$ m. These results confirm the long term pozzolanic reaction of Shirasu. The results also suggest that finer the particle size of Shirasu, larger is its surface area which increases the rate of pozzolanic reaction.

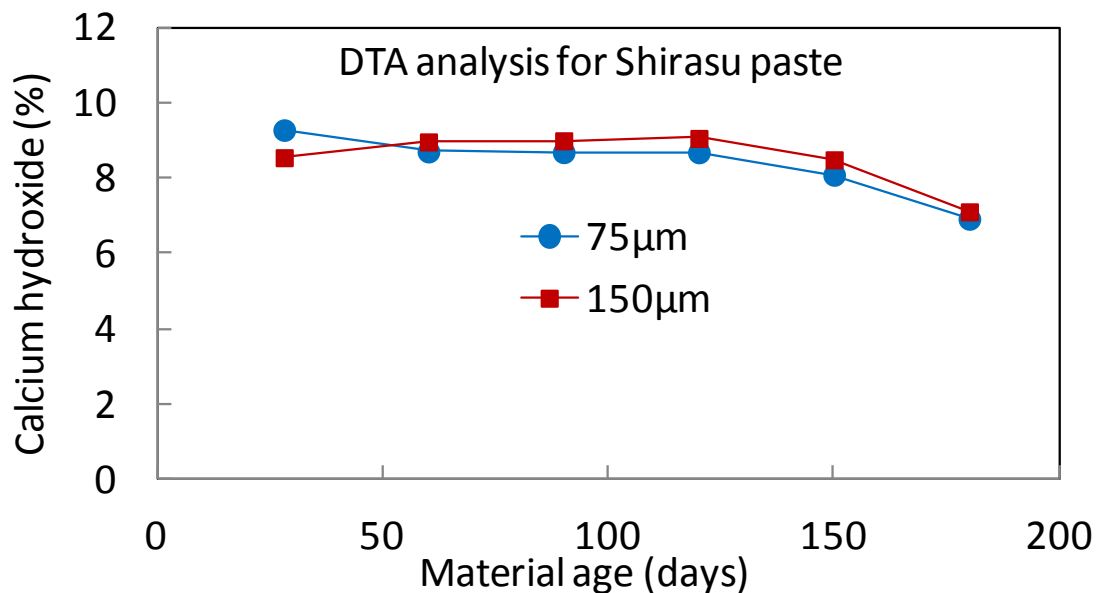


Fig. 3.35 Thermo-gravimetric analysis for both particle sizes of Shirasu

### 3.1.6 Summary

Two types of Shirasu and two types of fly ashes are employed in the research for better understanding the pozzolanic reactivity of Shirasu. Both Shirasu and fly ash have high content of silica and alumina and hence show pozzolanic reaction. Physical property of both the pozzolans differs. Shirasu is highly porous, on the other hand fly ash has

smooth spherical surface possessing ball bearing property. Due to high porous nature of Shirasu, it has high water absorption characteristics. Introduction of Shirasu in concrete as fine aggregate lowers the actual W/B which is attributable to its high water absorbing capacity. For this reason, tests on Shirasu mortar with alterations in water content based on water absorption percentage are done. The results confirmed that fine particles of Shirasu as binder do not affect water binder ratio unlike Shirasu used as fine aggregate. It is also evident that the altered Shirasu mortar not only gives good flow characteristics and workability for mortar but also long term strength gain by almost matching the strengths with that of ordinary mix proportion of Shirasu.

From the experimental results, the mortar in which 10% of cement content is replaced by Shirasu resulted in higher strength up to 1 year. The mortars with 20% and 30% replacement levels have slower rate of strength gain, but may gradually increase at longer duration of curing periods and match the strengths of 10% replacement. Increase in water-binder ratio, decreases the strength of mortar which is consistent with the theoretical results. Regardless of water to binder ratio, the strengths of Shirasu mortars increased at longer durations of curing period. Fly ash has higher reactivity and has higher strengths than the ordinary Portland cement mortar. On the other hand, Shirasu has lesser reactivity at early ages and increases in the long term. Due to long term pozzolanic reactivity of Shirasu, the strength of Shirasu mortar is expected to increase even more beyond 1 year of material age and in turn increase the service life and durability of concrete and structures. Hence, potential of Shirasu needs to be exploited as a cement replacement material contributing to utilization of unused natural resource and sustainable concrete.

## **3.2 Shirasu as Binder with Different Blaine Specific Surface Area**

### **3.2.1 General**

In the previous section (Section 3.1), pozzolanic reactivity of Shirasu is analyzed for fine particles of Shirasu of under 150 $\mu$ m. The fineness of particle used as binder (pozzolan) plays an important role in densifying the matrix, micro-filling effect and reactivity of binder. Reactivity of pozzolan increases as the surface area of particle available for reaction increases. Smaller the size of particle, larger the specific surface area of particle. Therefore, in this study pozzolanic reactivity of Shirasu is examined for different Blaine specific surface area of particles and different Shirasu replacement ratio as binder in mortar. The air permeability specific surface of a powder material is a single-parameter measurement of the fineness of the powder. The specific surface is derived from the resistance to flow of air (or some other gas) through a porous bed of the powder.

One of the simple methods to determine the fineness of particles is called Blaine specific surface area. Blaine method is now by far the most commonly used, mainly because of the ease of maintenance of the apparatus and simplicity of the procedure. Mortars with Shirasu as cement replacement material with Shirasu particles of different Blaine specific surface area (3000cm<sup>2</sup>/g, 5000cm<sup>2</sup>/g, and 7000cm<sup>2</sup>/g) and replacement ratios (5%, 10% and 30%) are cast. The compressive strength and bending strength of mortars are compared with each of different variants of Shirasu mortar and also with OPC mortar as control.

### 3.2.2 Materials

#### 1. Binders:

Ordinary Portland cement is used as one of the binders. Taniyama San Shirasu is used as binder (cement replacement material) with different Blaine specific surface area of particles and different Shirasu replacement ratio.

#### 2. Fine aggregate:

River sand is used as fine aggregate.

The physical characteristics of Taniyama San Shirasu are shown in Table 3.6. Fine particle fraction of Taniyama San Shirasu is high and water absorption is higher when compared to other types of Shirasu. Taniyama San Shirasu is also characterized by high percentages of silica and alumina in its mineral composition.

Table 3.6 Characteristics of Shirasu used

Type of Shirasu/location	Density of surface-dry state (g/cm <sup>3</sup> )	Absorption capacity ratio (%)	Fineness modulus	Fine powder ratio (%)
Taniyama San	2.06	11.31	1.53	21.9

### 3.2.3 Mix Proportions

Water cement ratio (“W/C”) is set at 65% for all mortars and water to aggregate ratio is fixed at 33%. Shirasu is used as binder with replacement ratios of 5%, 10% and 30%



and with different Blaine specific surface areas of 3000cm<sup>2</sup>/g, 5000cm<sup>2</sup>/g, and 7000cm<sup>2</sup>/g for each of the replacement ratios. OPC mortar with Ordinary Portland cement is made as control specimen for comparative study. Prism specimens of dimension 4\*4\*16cm<sup>3</sup> are cast.

Table 3.7 Mix proportion (unit weight, kg/m<sup>3</sup>)

W/C	Water/Aggregate	Blaine (cm <sup>2</sup> /g)	Replacement ratio (%)
65%	33%	7000	5
			10
			30
		5000	5
			10
			30
		3000	5
			10
			30

### Curing Condition and Experimental Test

The casted specimens are normal water cured for predetermined curing periods of 1, 2, 4, 13, 26 and 52 weeks and compressive strength and bending strength test for all mortars are carried out at each curing period up to 52 weeks of curing as per JIS 5201 standards.

### 3.2.4 Results and Discussion

#### Compressive strength of Shirasu mortars

The comparison of compressive strength between different Blaines of Shirasu for Shirasu replacement ratio of 30% is shown in Fig. 3.36. The strength of Shirasu mortar is lower compared to OPC up to 52 weeks of curing. However, among the Shirasu mortars, the strength of mortars increases as the Shirasu Blaine increases. Higher the Blaine value higher is the area of particles and lower the particle size. Therefore, the reactivity of Shirasu particles increases as fineness increase. As the replacement ratio of Shirasu increases in the mortar, the strength of Shirasu mortars decrease which is illustrated in Fig. 3.37 and Fig. 3.38. The compressive strength of all mortars with different replacement ratios and Blaine are less than OPC at early ages of curing. This is attributed to the fact that cement hydration is incomplete at early ages and availability of calcium hydroxide for pozzolanic reactivity of Shirasu is less. Also, at early ages of curing, the difference in strength between OPC and Shirasu increase as replacement ratio increases for all cases of Blaine values. In the case of Shirasu replacement ratio of 10%, mortars with Shirasu having Blaine value of  $7000 \text{ cm}^2/\text{g}$  and  $5000 \text{ cm}^2/\text{g}$  have higher compressive strength than OPC at 52 weeks of curing period. But, mortar with Shirasu having Blaine value of  $3000 \text{ cm}^2/\text{g}$  has slightly lesser compressive strength than OPC. In the case of Shirasu replacement ratio of 5%, all Shirasu mortars have higher compressive strength than OPC at longer curing periods. This result is attributed to the fact that, as replacement ratio increase, there is relative reduction of amount of cement in the mixture.

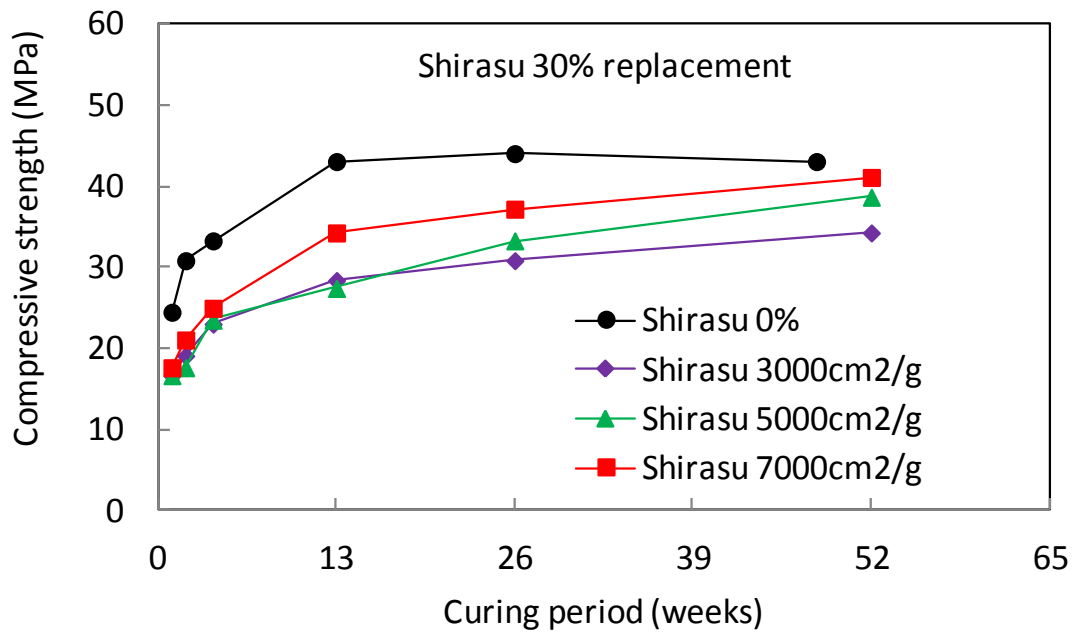


Fig. 3.36 Compressive strength comparison between different Blaines for Shirasu replacement ratio of 30%

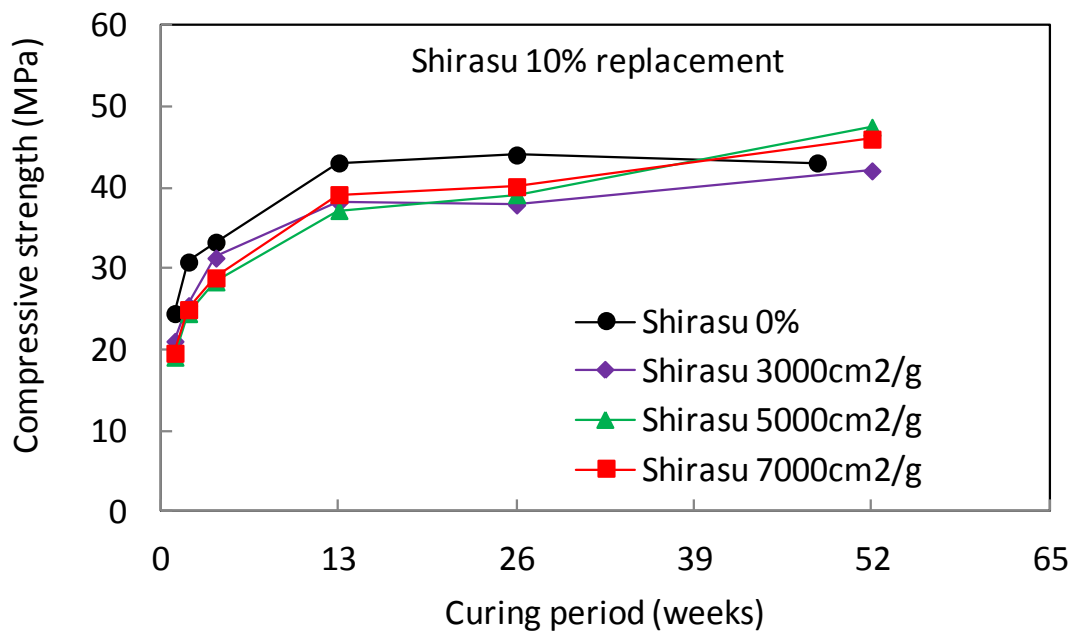


Fig. 3.37 Compressive strength comparison between different Blaines for Shirasu replacement ratio of 10%

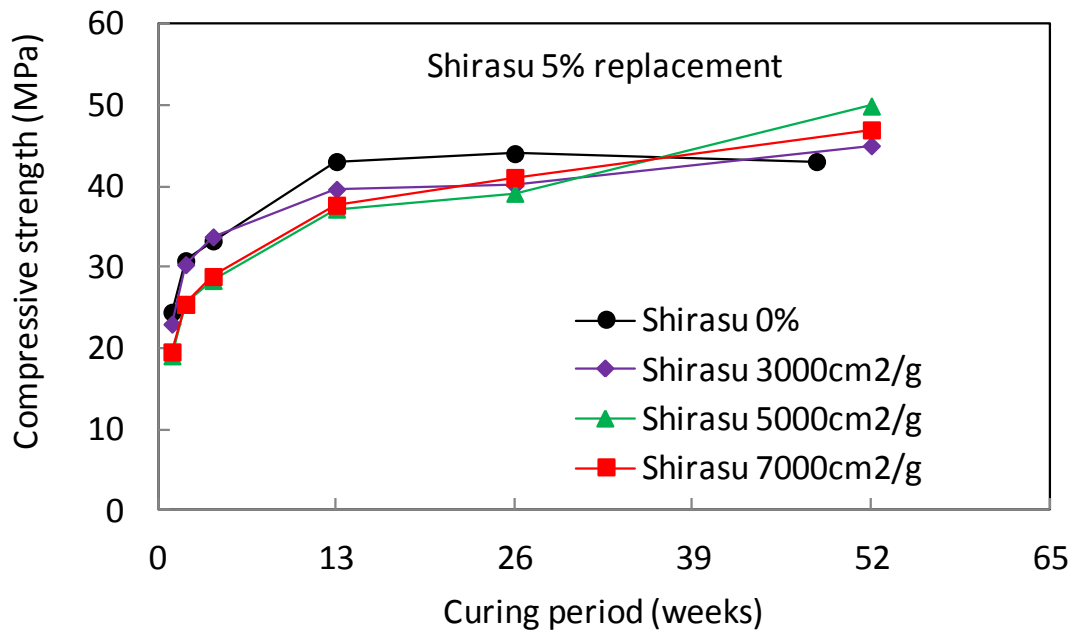


Fig. 3.38 Compressive strength comparison between different Blaines for Shirasu replacement ratio of 5%

Therefore there is reduction in absolute amount of  $\text{Ca}(\text{OH})_2$  produced by cement hydration. This condition will affect the reactivity of Shirasu and consequently reduces the strength as illustrated in Fig. 3.39, Fig. 3.40 and Fig. 3.41 which represent the comparison of compressive strength between different Shirasu replacement ratios for each Blaine value of Shirasu in mortar. At early ages of curing, the difference in compressive strength between OPC and Shirasu mortars increase as the Blaine decreases for all replacement ratios. In all the cases of Blaine specific surface area of Shirasu, mortars having replacement ratio of 5% and 10% have higher or almost same compressive strength as OPC at longer durations of curing. But, mortars with replacement ratio of 30% have lesser compressive strength regardless of Blaine.

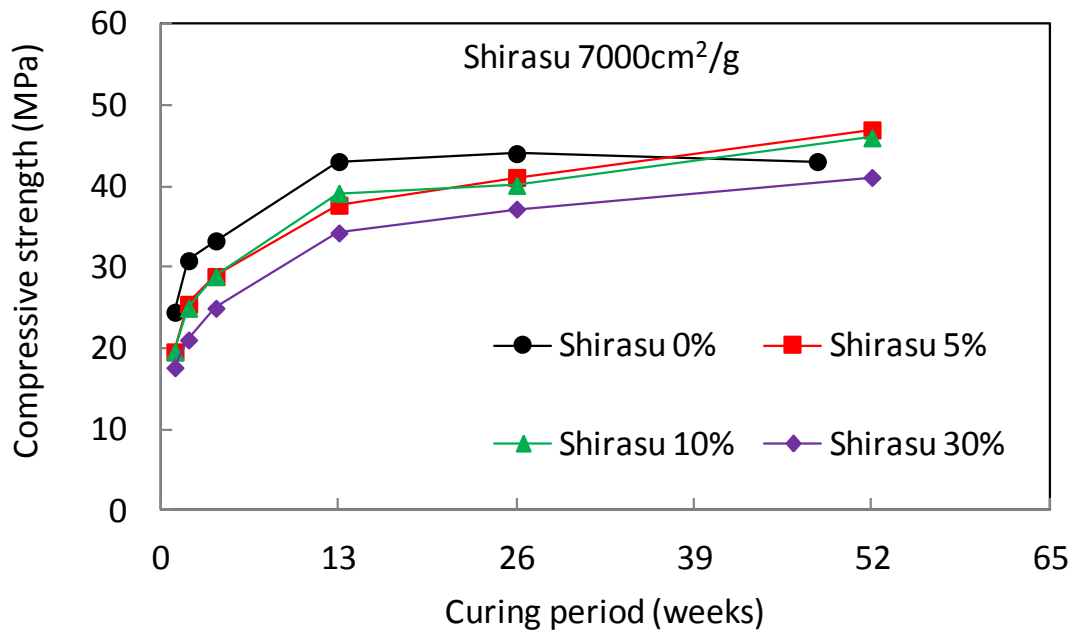


Fig. 3.39 Compressive strength comparison between different replacement ratios of Shirasu having Blaine 7000cm<sup>2</sup>/g

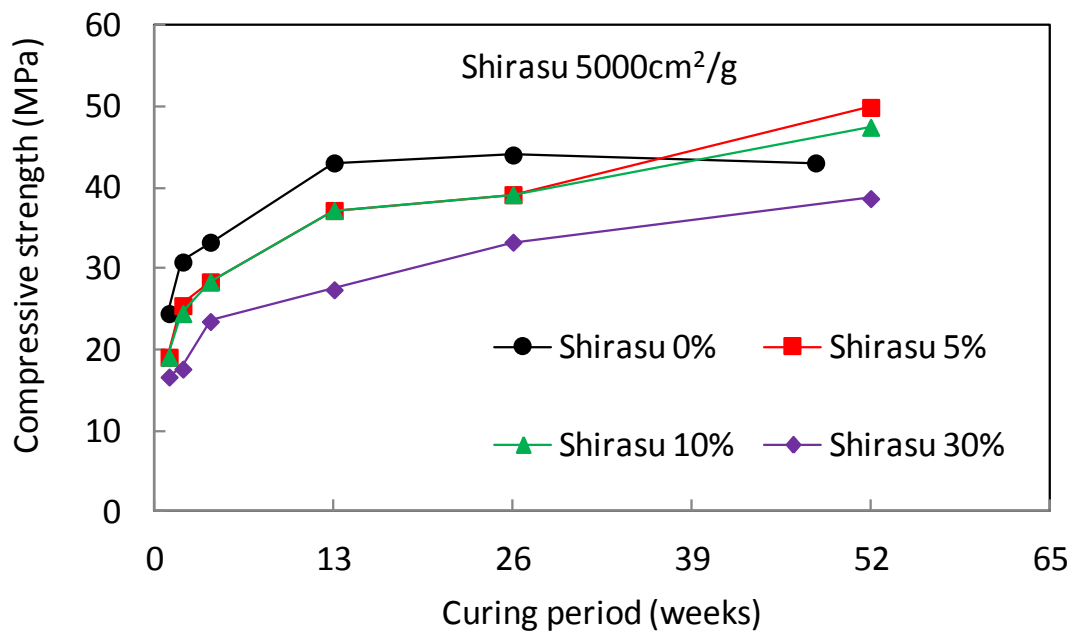


Fig. 3.40 Compressive strength comparison between different replacement ratios of Shirasu having Blaine 5000cm<sup>2</sup>/g

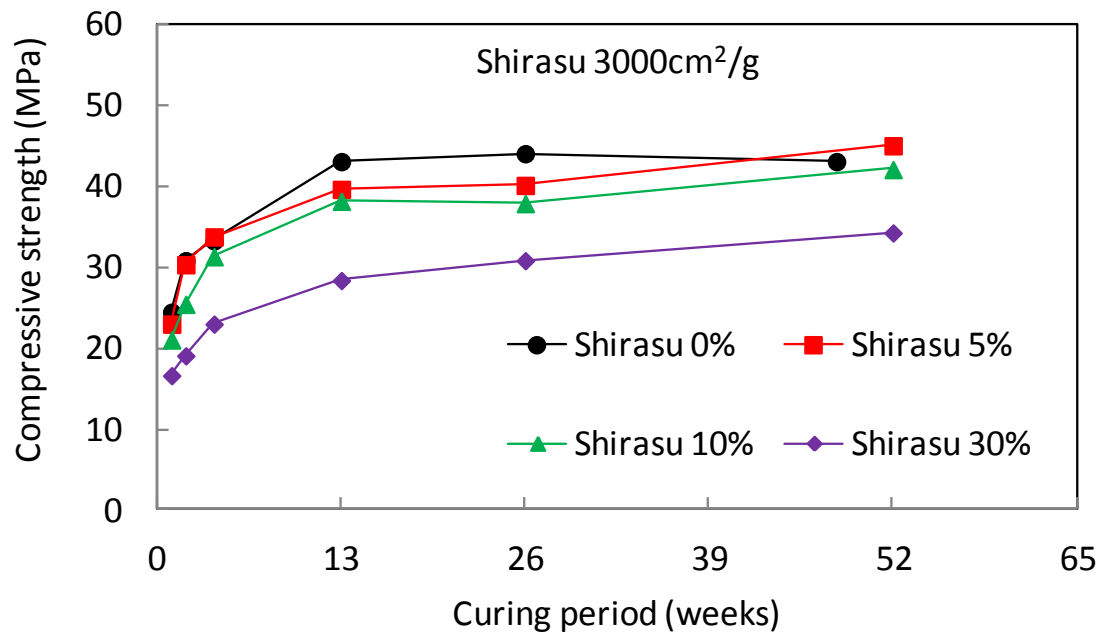


Fig. 3.41 Compressive strength comparison between different replacement ratios of Shirasu having Blaine 3000cm<sup>2</sup>/g

Shirasu mortar with Blaine of 7000cm<sup>2</sup>/g is almost similar to OPC after 1 year even though the replacement ratio is 30%. This confirms the long term pozzolanic reactivity of finer Shirasu particles.

### Percentage increment in compressive strength

To examine the rate of pozzolanic reaction of Shirasu in Shirasu mortar, percentage increment in compressive strength with age is calculated. Percentage increment in compressive strength versus the curing period of Shirasu mortars with different Blaine specific surface area of Shirasu particles is illustrated in Fig. 3.42, Fig. 3.43 and Fig. 3.44 for different replacement ratios respectively.

The percentage increment in compressive strength is higher in case of replacement ratio

of 5% and decreases as the replacement ratio increases. At early ages of curing, percentage increment in compressive strength of Shirasu mortars is almost same or less than OPC. But at longer durations of curing period, percentage increment in compressive strength of Shirasu mortars are clearly higher than OPC for replacement ratio of 30%.

Percentage increment in compressive strength of Shirasu mortars is higher at all ages for replacement ratios of 5% and 10% regardless of Blaines. For all replacements ratios, mortars with Shirasu Blaines of  $7000\text{cm}^2/\text{g}$  and  $5000\text{cm}^2/\text{g}$  have higher percentage increment in compressive strength at all ages. These results confirm that the reactivity increases with increase in specific surface area regardless of replacement ratio.

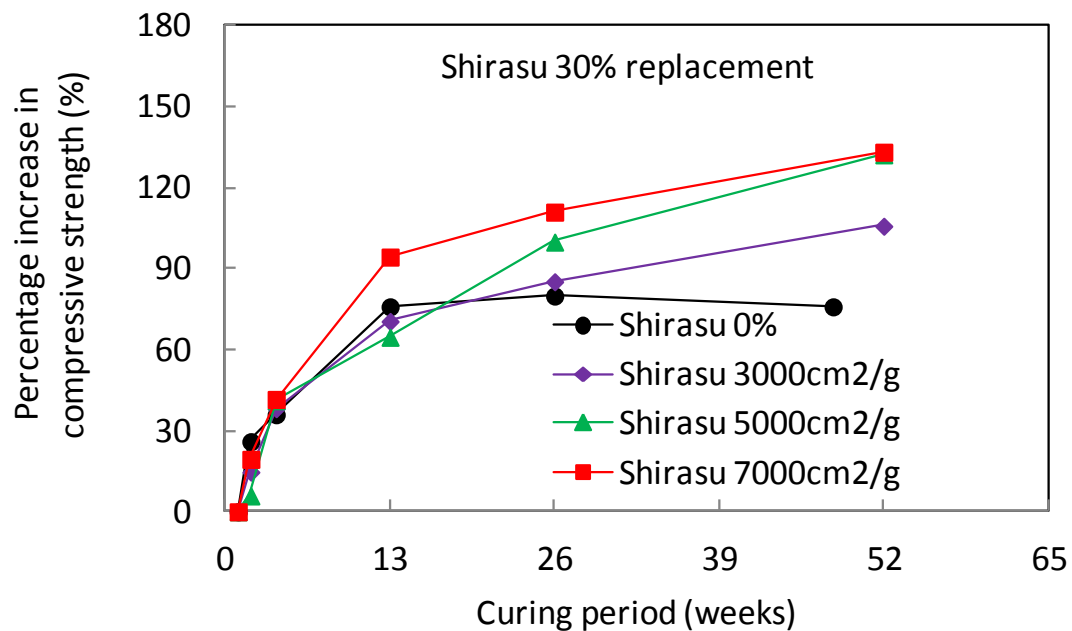


Fig. 3.42 Percentage increase in compressive strength between different Blaine of Shirasu for replacement ratio of 30%

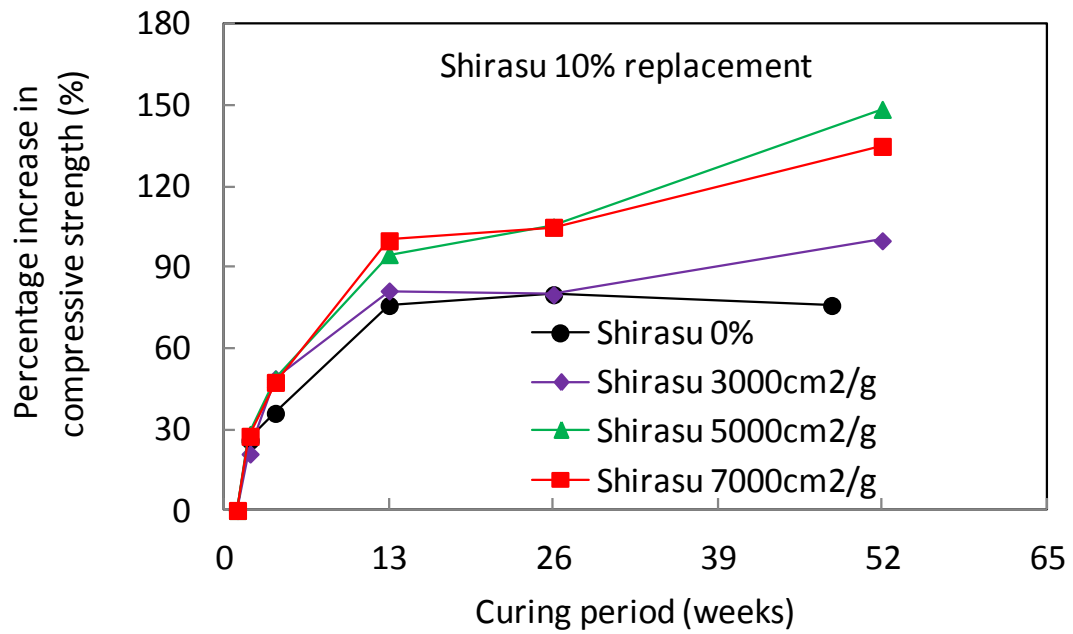


Fig. 3.43 Percentage increase in compressive strength between different Blaine of Shirasu for replacement ratio of 10%

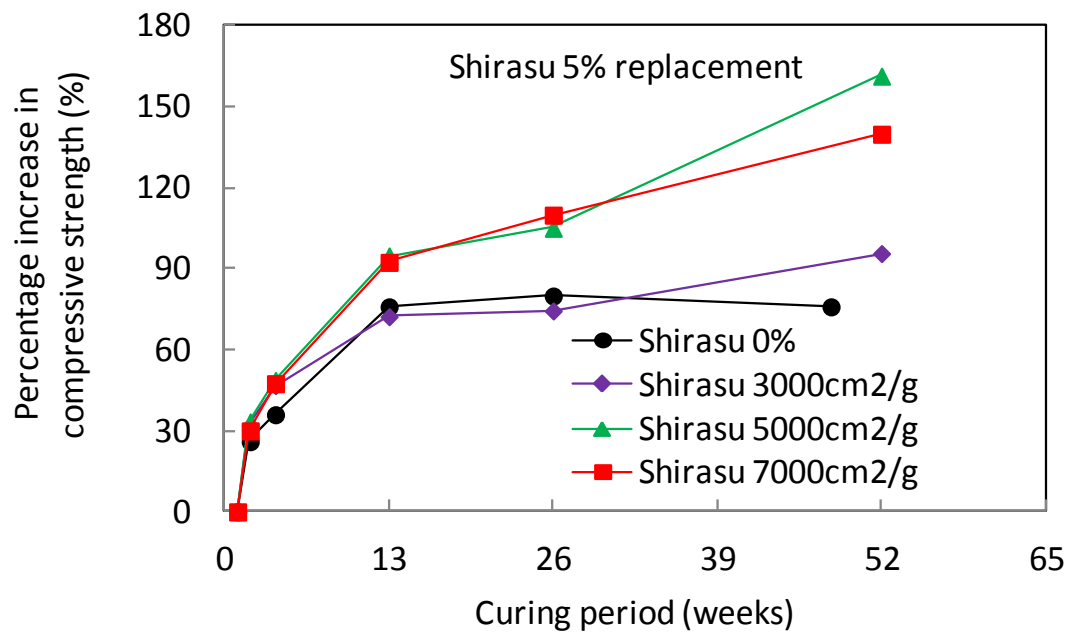


Fig. 3.44 Percentage increase in compressive strength between different Blaine of Shirasu for replacement ratio of 5%



### Bending strength of Shirasu mortars

The bending strengths of all mortars with Shirasu Blaines of 3000cm<sup>2</sup>/g, 5000cm<sup>2</sup>/g, and 7000cm<sup>2</sup>/g are shown in Fig. 3.45, Fig. 3.46 and Fig. 3.47 in comparison with different replacement ratios. For all replacement ratios and Blaines of Shirasu, the flexural strength is lesser than OPC mortars up to 26 weeks. Especially for replacement ratio of 5%, the flexural strength of all Blaine values of Shirasu in Shirasu mortar is equal or slightly higher than OPC at 1 year curing. On the other hand, for replacement ratios of 10% and 30%, flexural strength drops at 1 year and significantly lesser than OPC.

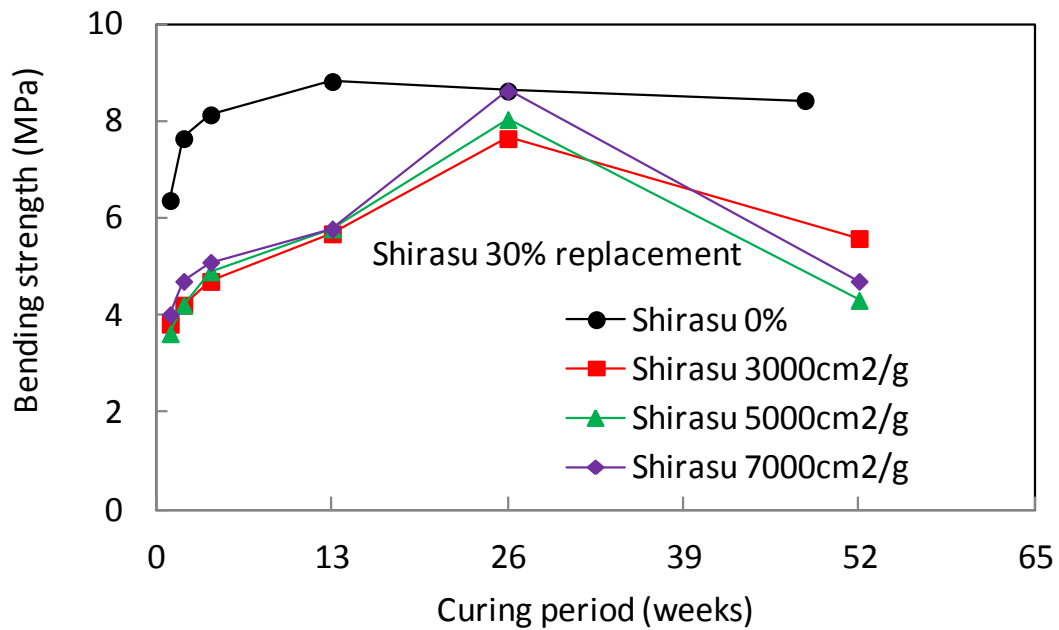


Fig. 3.45 Bending strength comparison between different Blaines for Shirasu replacement ratio of 30%

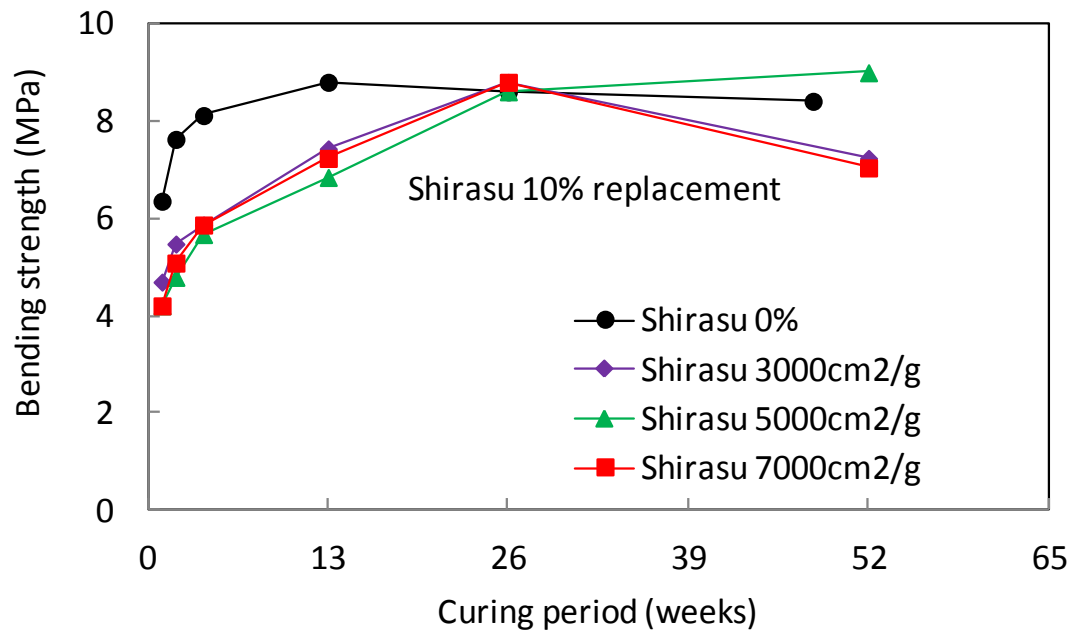


Fig. 3.46 Bending strength comparison between different Blaines for Shirasu  
replacement ratio of 10%

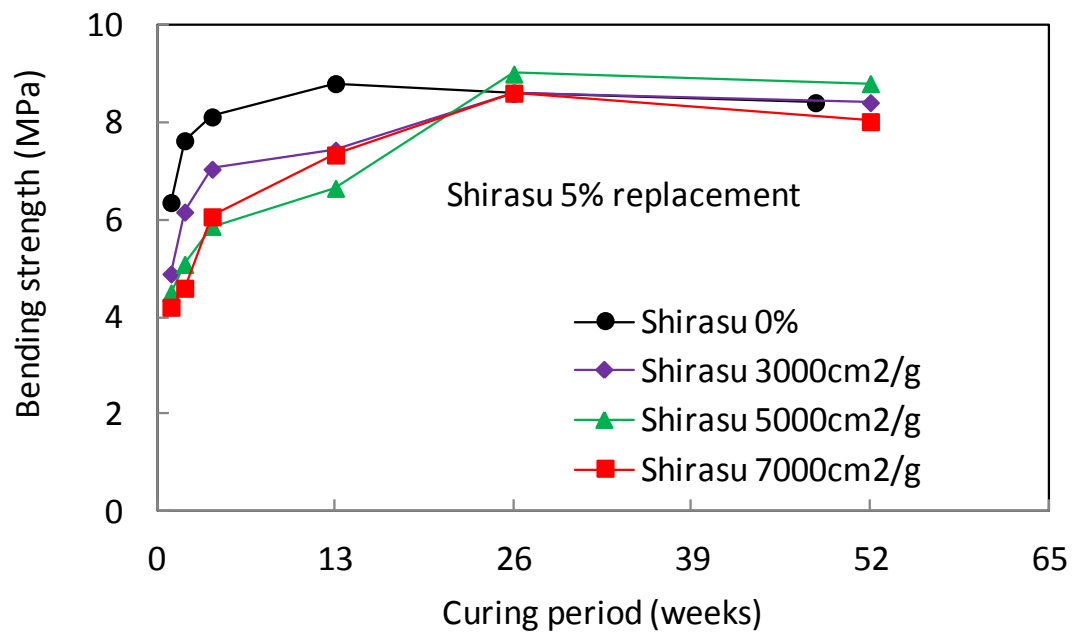


Fig. 3.47 Bending strength comparison between different Blaines for Shirasu  
replacement ratio of 5%

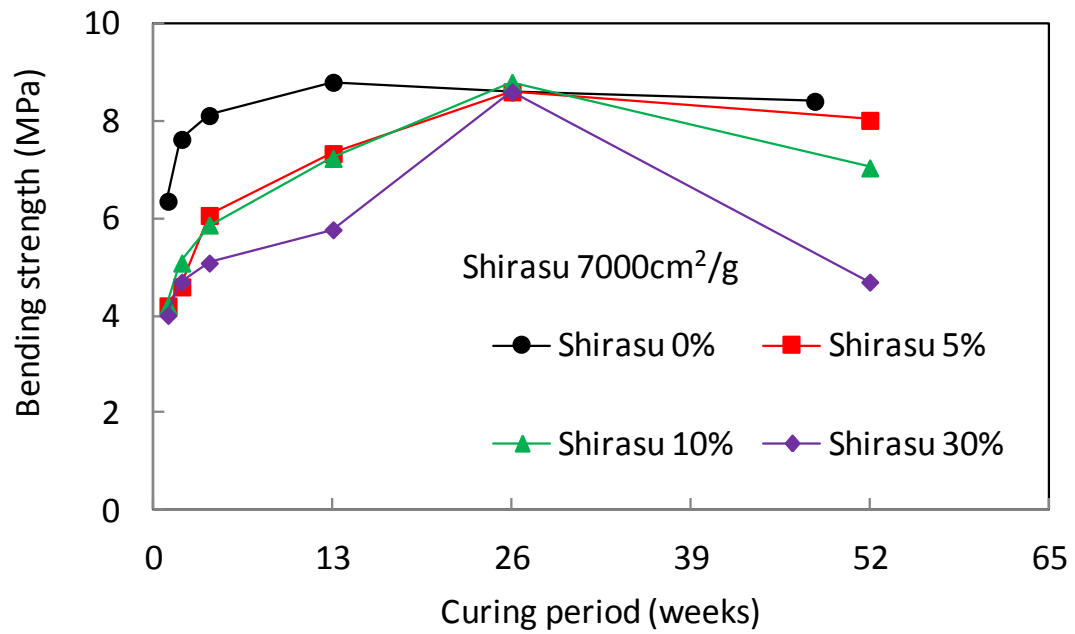


Fig. 3.48 Bending strength comparison between different replacement ratios of Shirasu having Blaine 7000cm<sup>2</sup>/g

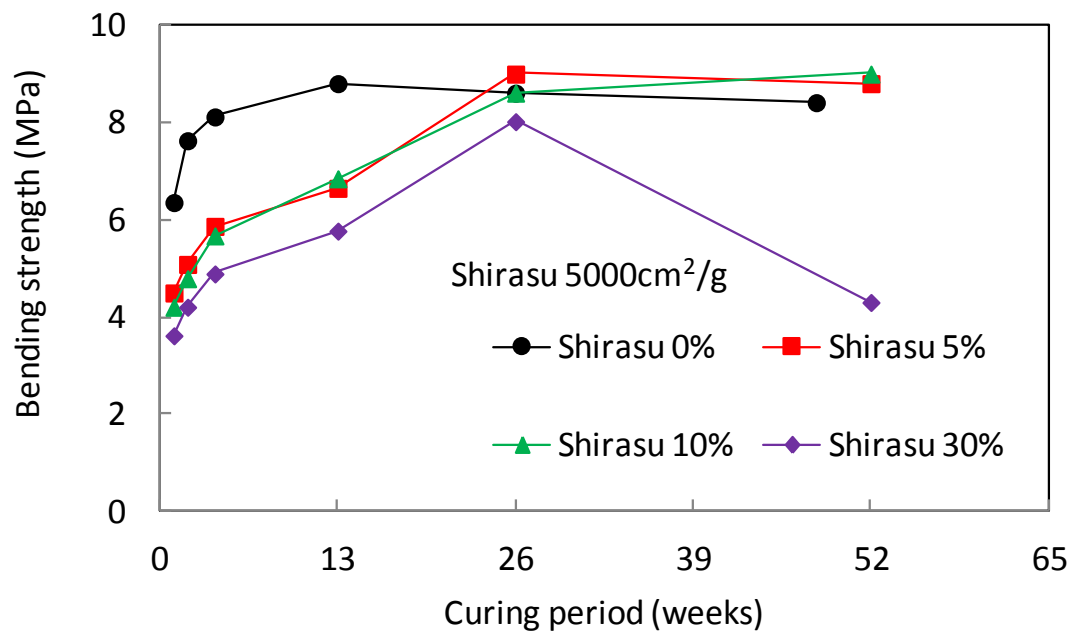


Fig. 3.49 Bending strength comparison between different replacement ratios of Shirasu having Blaine 5000cm<sup>2</sup>/g

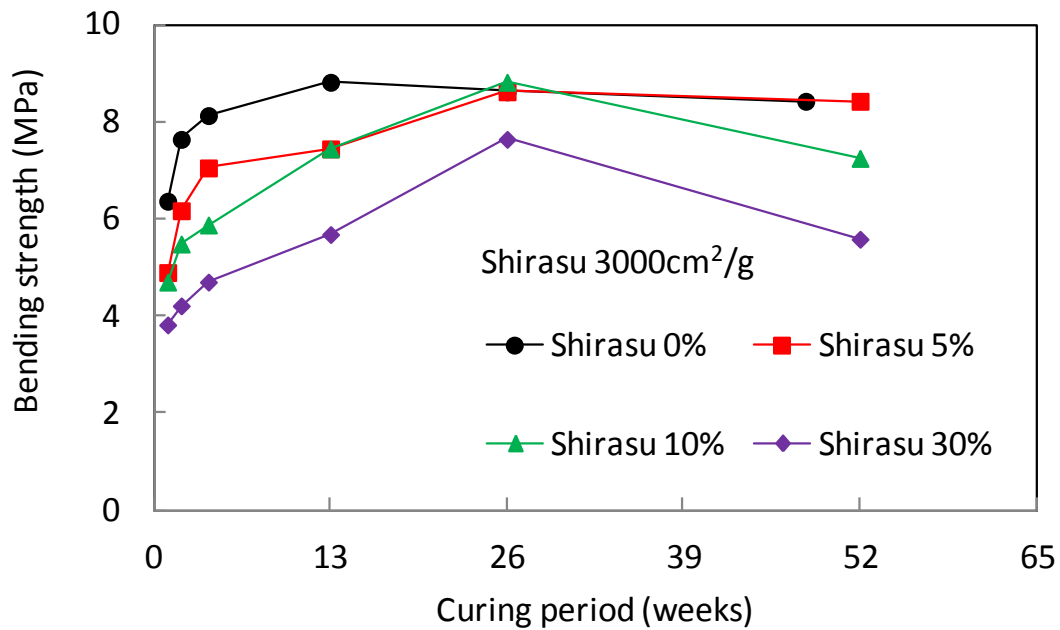


Fig. 3.50 Compressive strength comparison between different replacement ratios of Shirasu having Blaine 3000cm<sup>2</sup>/g

Observing the bending strength difference between replacement ratios for each Blaine of Shirasu (illustrated in Fig. 3.48, Fig. 3.49 and Fig. 3.50), the strength is almost equal to OPC for mortars with Shirasu replacement of 5% and 10% at the age of 26 weeks. At longer ages of curing, mortar with 5% replacement is almost same or higher than OPC in some cases.

### 3.2.5 Summary

Shirasu as binder with different Blaine specific surface area and replacement ratio in mortar showed good pozzolanic reactivity at longer durations of curing. Finer Shirasu particles (higher value of Blaine) have higher reactivity even when the replacement ratio is as high as 30%. Therefore, fineness of Shirasu particles is an important factor to be

considered when using Shirasu as cement replacement material. Even though increase in replacement of Shirasu decreases the strength, the strength is almost similar to OPC when the Blaine is  $7000\text{cm}^2/\text{g}$ . Replacement as high as 30% is possible if the fineness of Shirasu particle is higher. The strength of mortars in some cases is higher than OPC even when the water cement ratio is 65%. Therefore, higher specific surface area of binder increases the reactivity resulting in denser concrete.

From the experimental results, it is expected that Shirasu can be used as binder with higher replacement ratios without affecting the properties of concrete by increasing the specific surface area of particles. The results of this study are consistent with the results of Shirasu as binder with size of under  $150\mu\text{m}$  explained in section 3.1. Especially, the compressive strength trends for Shirasu Blaine specific surface area of  $3000\text{cm}^2/\text{g}$  are similar to that of strength trends of Shirasu under  $150\mu\text{m}$  as binder in mortar illustrated in section 3.1. Development of strength is higher for higher specific surface area of particles.

Higher fineness of binders increases the surface area available for reaction, hence increase the reactivity. At the same time, finer particles need more water to wet the surface. This increases water demand. In the experimental results on variation in Blaine specific surface area and replacement ratios, Shirasu replacement of 30% with Blaine value of  $7000\text{cm}^2/\text{g}$  had almost same compressive strength compared to OPC mortar. Lower replacement ratios had higher compressive strength than the OPC for less finer Shirasu also. But replacement of 30% is possible to have fairly good compressive strength equal to OPC with higher fineness.

Higher replacement ratio than 30% can make concrete stiffer and also higher water demand for attaining good workability. Higher replacement of cement than 30% reduces total amount of cement and consequently reduce absolute amount of  $\text{Ca(OH)}_2$ . This reduces the total pH maintained in the matrix and reduces the rate of dissolution of silica and alumina from Shirasu. It results in lesser reactivity of Shirasu and subsequently reduces strength. Higher replacement of Shirasu can be employed in the mix where structures do not need higher strengths at much early age.

## **Chapter 4**

### **PERMEABLE PAVEMENT**

#### **4.1 Permeable Pavement Using Shirasu as Fine Aggregate and Recycled Gypsum as Binder**

##### **4.1.1 General**

Permeable pavement is a sustainable material and technique that allows the movement of storm water through the surface, reducing runoff. Several researches on permeable pavement and their materials have been done in the past using sand as fine aggregate. Permeable pavements using sand as fine aggregate are being commercially used worldwide with wide range of applications like pathways, parking areas, disposal yards for collection of leachates etc. Suitable proportioning and grading of materials improves the quality of pavement. Shirasu, which is highly porous, is known to have pozzolanic reaction. Utilization of Shirasu as fine aggregate may improve the quality of pavement by having sufficient strength property and permeability. An attempt to use both recycled waste like gypsum and Shirasu which is unused natural resource is tried in this study by suitably proportioning the materials in mortar to produce permeable pavements.

Two types of Shirasu are used as fine aggregates. In case of mix proportions with variation in gypsum, percentage of Shirasu is maintained at 75% of total weight of mixture while the gypsum/binder is varied. In addition, the mix proportions in which gypsum/binder is kept constant at 15% and Shirasu percentage is varied from total

mixture are also done. Strength and permeability test results are compared with target values of 3.8MPa of compressive strength and  $5 \times 10^{-5}$  cm/s of permeability. These target values are based on experimental investigation done on commercial materials for good permeable pavement to obtain the optimum replacement levels of gypsum and Shirasu ratio.

#### **4.1.2 Materials**

Ordinary Portland cement (here-in-after called “OPC”) and High Early Strength Portland Cement (here-in-after called “HPC”) are used for comparative study.

Gypsum of specific gravity 2.49 is used as one of the binders with different percentages of total amount of binder containing OPC or HPC. Crushed plasterboards are recycled and burnt at temperatures of  $180^{\circ}\text{C}$ . The product is  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$  which is used as binder, replacing cement partially. The above compound contains very little paper and impurities which is advantageous.

Two types of Shirasu are used as fine aggregate. Table 4.1 shows the properties of Shirasu used. Yokogawa Shirasu and Koriyama Shirasu have high water absorption capacity and similar in density. But, Yokogawa Shirasu has higher fine particle fraction than Koriyama Shirasu. Therefore, Yokogawa Shirasu is expected to have higher long term pozzolanic reactivity than Koriyama Shirasu.



Table 4.1 Properties of Shirasu used

Shirasu type	Specific gravity	Water absorption (%)	Fine particle fraction
Yokogawa	2.18	7.52	21.25
Koriyama	2.17	7.58	16.9

#### 4.1.3 Mix Proportions for Mortar

The percentage of Shirasu is maintained at 75% of total weight of mixture while the gypsum percentage from total binder (gypsum+cement) percentage is varied as shown in Table 4.2. In addition, post analysis of permeable pavements based on mix proportions shown in Table 4.2, the optimum gypsum/binder is selected and mix proportions in which gypsum/binder percentage is kept constant at 15% and the Shirasu percentage is varied from total mixture, as shown in Table 4.3, are also prepared for the examination. All the mix proportions are on weight basis.

Table 4.2 Mix proportion with variation in gypsum

Gypsum/Binder (%)	Gypsum (kg)	Cement (kg)	Shirasu (kg)
5	12.5	237.5	750
10	25	225	
15	37.5	212.5	
20	50	200	
30	75	175	

Table 4.3 Mix proportion with variation in Shirasu

Shirasu content (%)	Shirasu (kg)	Cement (kg)	Gypsum (kg)
95	950	42.5	7.5
90	900	85	15
85	850	127.5	22.5
80	800	170	30
75	750	212.5	37.5
70	700	255	45
65	650	295.5	52.5
60	600	340	60

#### 4.1.4 Preparation of Mortar

Preparation method of mortar is based on standards of permeable pavements. In the case of pavements practically used worldwide, gravel is laid on the ground initially to make a firm bed. Next, the pavement materials without water are mixed in advance and laid on the gravel base. Then water is sprayed on it. Similar curing technique is followed in the research to simulate the actual condition. Spraying large amount of water on mass pavement would result in formation of air pockets. Therefore, sufficient amount of water required is sprayed at regular intervals on the specimens after casting the materials. Sequences of spraying water are as follow:

1<sup>st</sup> stage: Water sprayed soon after casting.

2<sup>nd</sup> stage: Water sprayed after 1.5hours of 1<sup>st</sup> stage.

3<sup>rd</sup> stage: Water sprayed after 1 day and 2 days after casting.

Normally, 1<sup>st</sup> and 2<sup>nd</sup> stages of water are used for the cement hydration and reaction of gypsum with water to make the mass stiffer. The 3<sup>rd</sup> stage of water spraying is normally for curing purpose.

Amount of water at each stages of spraying is based on standards for water curing for pavements and is given in Table 4.4.

Table 4.4 Standard amount of water for curing

1st stage (kg/m <sup>2</sup> )	2nd stage (kg/m <sup>2</sup> )	1day and 2 days (kg/m <sup>2</sup> )
3.45	6.96	9.24

#### 4.1.5 Specimen Setup

Two types of specimens are made for strength test and permeability test and their setup are shown in Fig. 4.1 and Fig. 4.2 respectively. For compressive strength and bending strength tests, prism specimens of dimensions 4\*4\*16cm<sup>3</sup> are cast and laid on wire mesh and net arrangement as shown in the figure. In the case of permeability test cylindrical specimens of diameter 10cm and length 5cm are cast and laid on wire mesh and net arrangement as depicted in the figure.

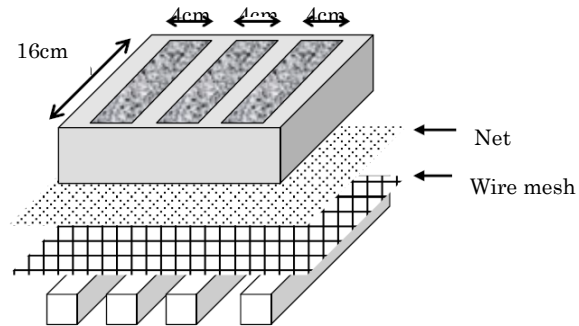


Fig. 4.1 Specimens for compressive strength and bending strength tests

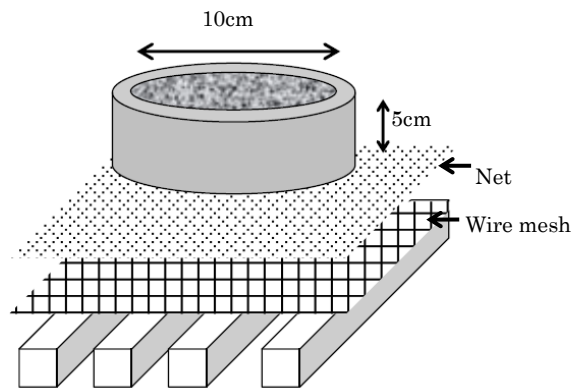


Fig. 4.2 Specimen for permeability test

#### 4.1.6 Permeability Test

Permeability test is carried out by gluing a 10cm PVC pipe of inner diameter 10cm on top of specimen casted for permeability test (Fig. 4.2) as shown in Fig. 4.3, in which water is filled and the constant head is maintained throughout the experiment for 2 hours. For every 30 minutes interval, the water passing through the specimen is collected and measured.

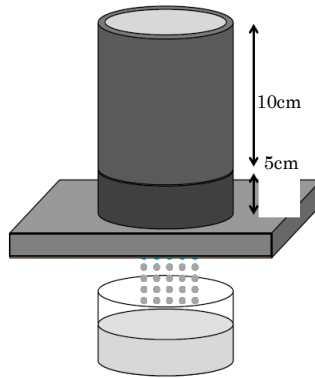


Fig. 4.3 Permeability test setup

Permeability coefficient is calculated using the Eq. (4.1) stated below:

$$Q = k (h/L) A \quad (4.1)$$

Where,

Q: flow rate,  $\text{cm}^3/\text{s}$

K: coefficient of permeability,  $\text{cm/s}$

h: water head,  $\text{cm}$

L: specimen height,  $\text{cm}$

A: area of cross-section of specimen,  $\text{cm}^2$

#### 4.1.7 Results and Discussion

##### Effect of variation in gypsum replacement ratio

Mortar specimens using Yokogawa Shirasu with mix proportion shown in Table 4.2 are examined for compressive strength, bending strength and permeability.

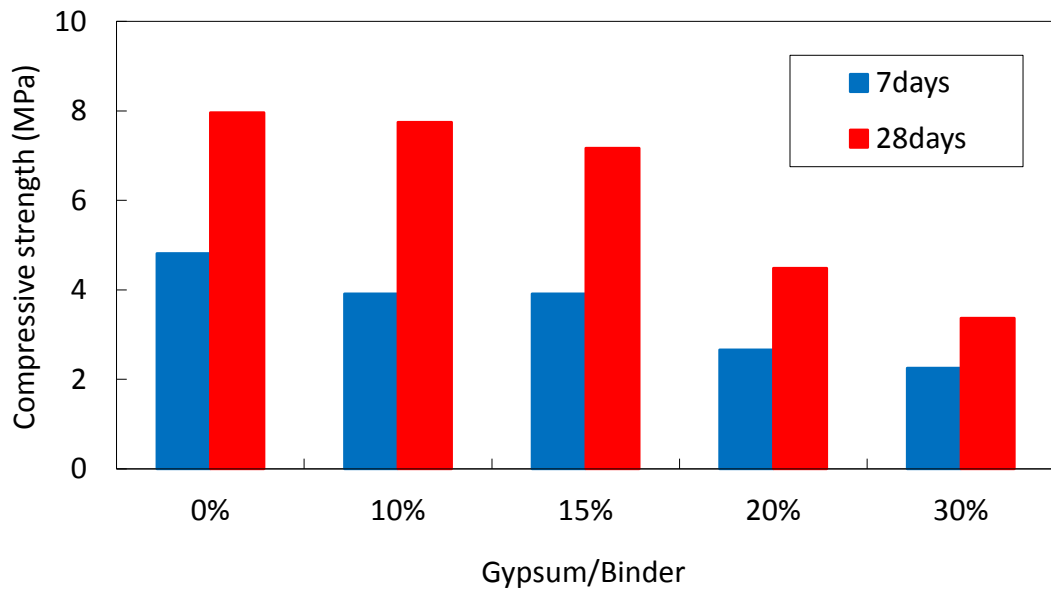


Fig. 4.4 Compressive strength of mortar with variation in gypsum

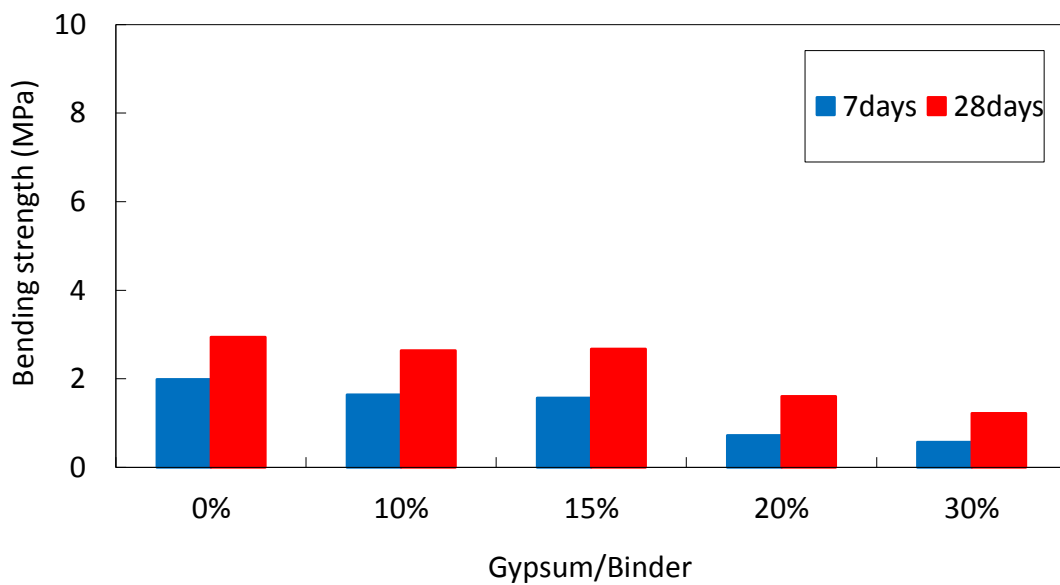


Fig. 4.5 Bending strength of mortar with variation in gypsum

As shown in Fig. 4.4 and Fig. 4.5, strengths decrease as replacement ratio of gypsum increases. This is because of reduction of cement ratio in mixture.

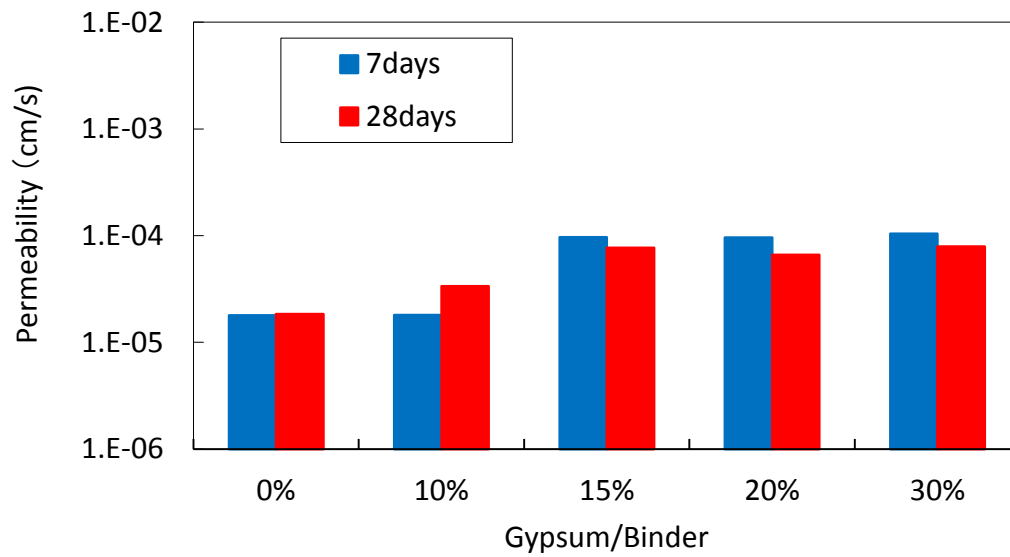


Fig. 4.6 Permeability of mortar with variation in gypsum ratio

Within 15% of gypsum replacement ratios, however, strength is not varying much and meets the required target strength of the experiment. On the other hand, permeability seems to increase with increment of replacement ratio, as shown in Fig. 4.6, though there is not much change in the range that the gypsum replacement ratio is larger than 15%. Therefore, the target value for permeability can also be attained at 15% replacement ratio.

#### **Effect of variation in Shirasu ratio**

In the examination on strength due to variation in gypsum ratio, it is clear that both strength and permeability of the mortar using gypsum and Shirasu reach their target value when gypsum/binder ratio is 15% or more. Therefore, in the experiment, mortar specimens having 15% of gypsum ratio kept as constant in the mix, of which mix proportions are given in Table 4.3, were examined.

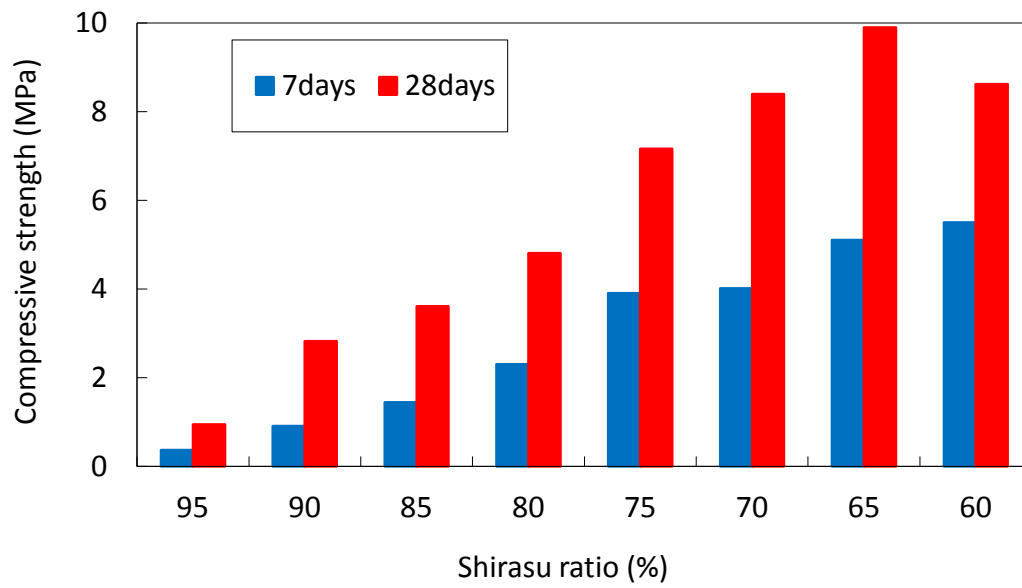


Fig. 4.7 Compressive strength of mortar with variations in Shirasu ratio

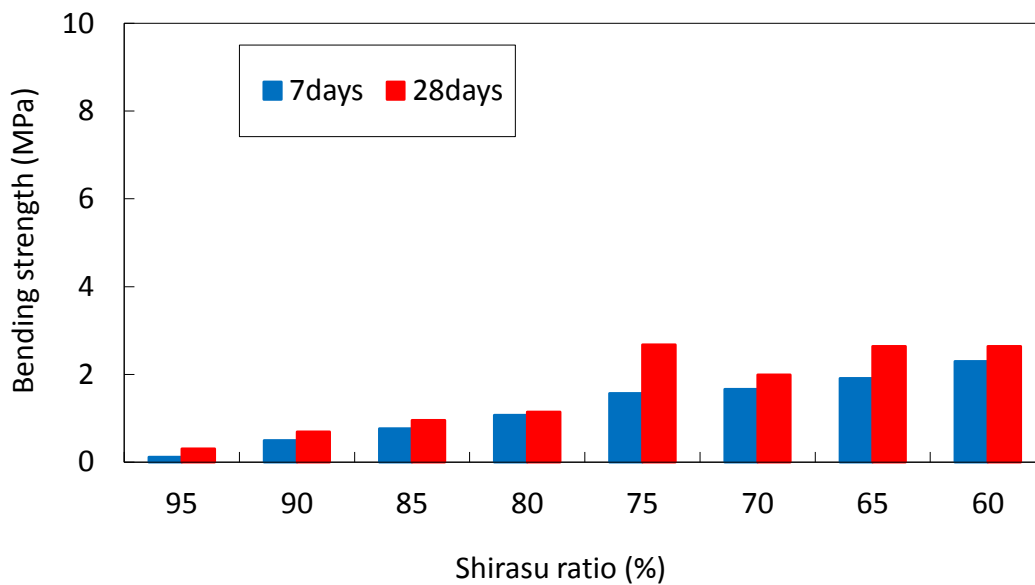


Fig. 4.8 Bending strength of mortar with variation in Shirasu ratio

Fig. 4.7 and Fig. 4.8 respectively show compressive and bending strengths of the mortars using Yokogawa Shirasu. They clearly show that the strengths increase with decrease in Shirasu ratio.



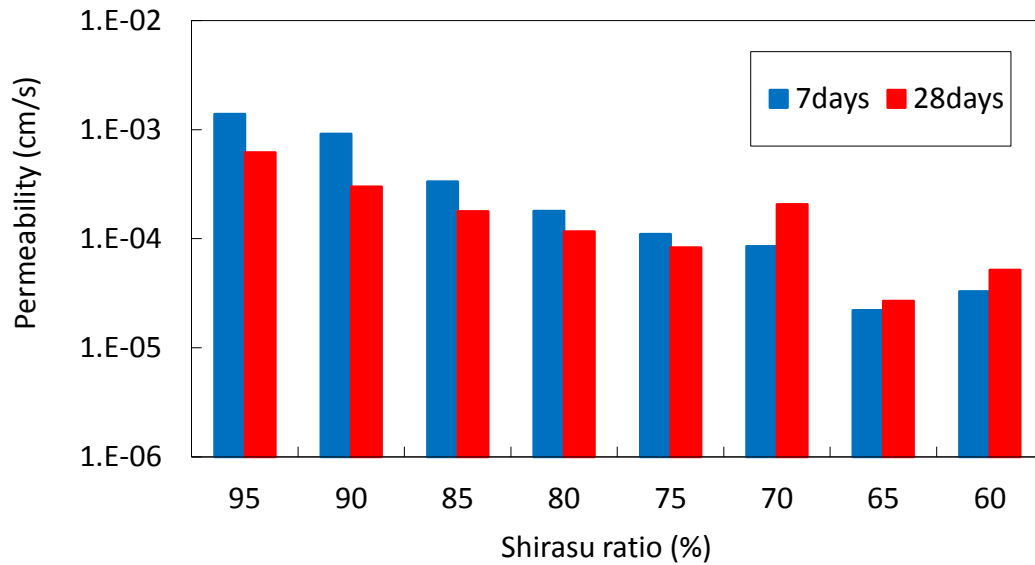


Fig. 4.9 Permeability of mortar with variation in Shirasu ratio

It is definitely due to relative increment in binder content. Also, the target value of the strength is reached at the mortars with 70% or less of Shirasu ratio after 7 days of curing. On the other hand, as the permeability seems to decrease with decrement of Shirasu ratio in the mortar as shown in Fig. 4.9, the target value of Shirasu ratio in the mortar should be a range between 70% and 75%.

### Effect of Shirasu type

An attempt is also made to examine the mortar using another type of Shirasu, called Koriyama Shirasu, with the same mix proportion used as in case of Yokogawa Shirasu (Table 4.3). From Fig. 4.10 and Fig. 4.11, the strength trends are same compared to the mortar using Yokogawa Shirasu and, the target value is achieved at 70% of Shirasu ratio after 7 days of curing and 80% of Shirasu ratio at 28 days curing. On the contrary, as shown in Fig. 4.12, the permeability is different from the case using Yokogawa

Shirasu.

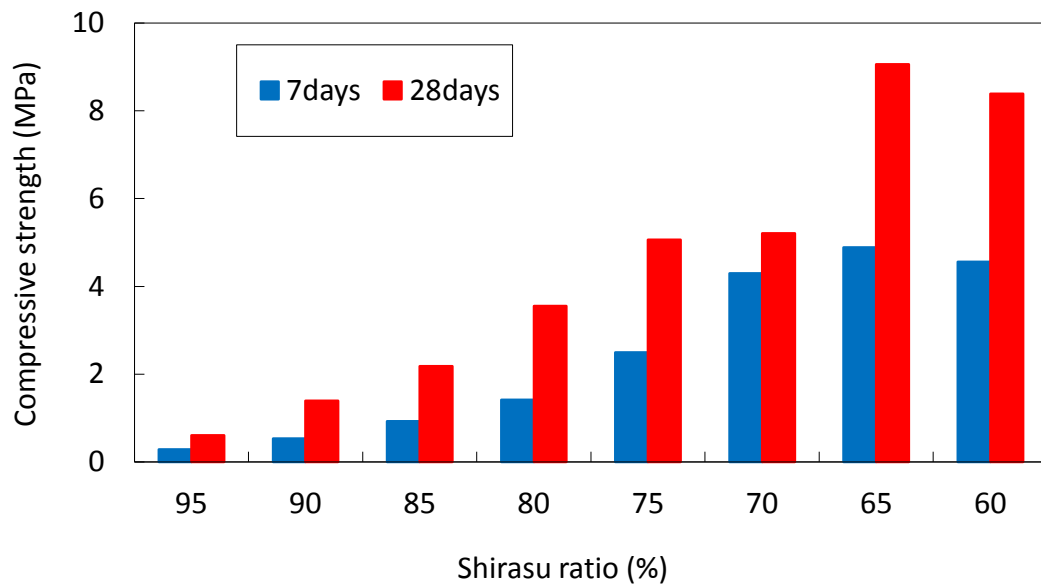


Fig. 4.10 Compressive strength of mortar with variation in Shirasu ratio (in case of using Koriyama Shirasu)

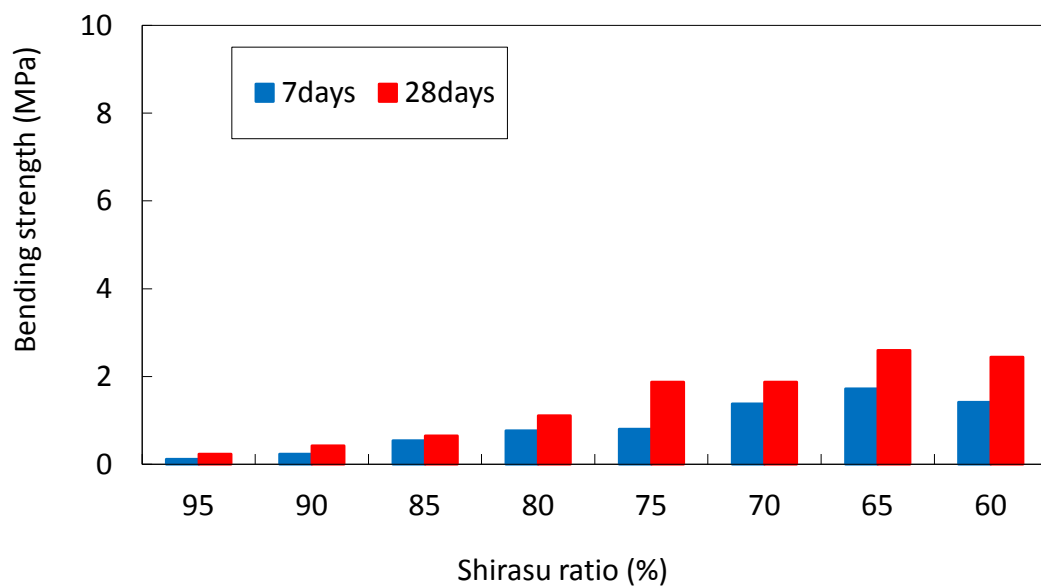


Fig. 4.11 Bending strength of mortar with variation in Shirasu ratio (in case of using Koriyama Shirasu)

The target value reaches straight away from 60% of Shirasu ratio to higher levels.

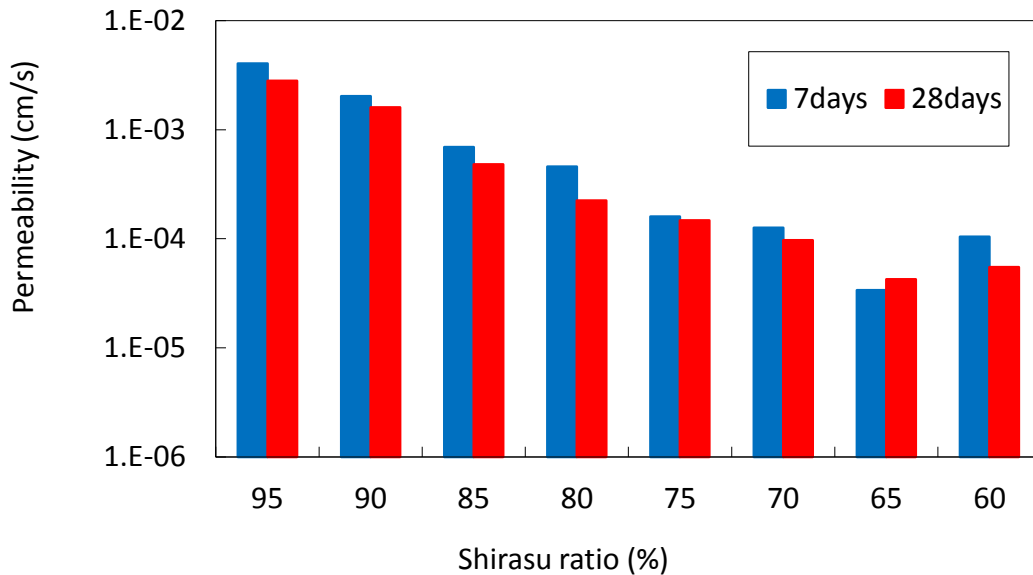


Fig. 4.12 Permeability of mortar with variation in Shirasu ratio (in case of using Koriyama Shirasu)

### Effect of cement type

A comparative study on mortars using OPC or HPC respectively has been done with mix proportion shown in Table 4.3. Here, only the results compared with binder (gypsum+cement) ratio up to 35% are shown. In Fig. 4.13, it is clearly shown that mortars using HPC shows higher compressive strength than the ones with OPC due to the fact that HPC has higher early strength compared to OPC. On the contrary, strength at 28 days, in Fig. 4.14, does not differ much proving that the long term strength of HPC is almost same as OPC even though the early strength is higher. At 7 days, HPC mortar reaches the target value at 15% binder ratio and OPC at 25% binder ratio. It is purely an advantage that target value reached at much lower binder ratio is contributed by HPC.

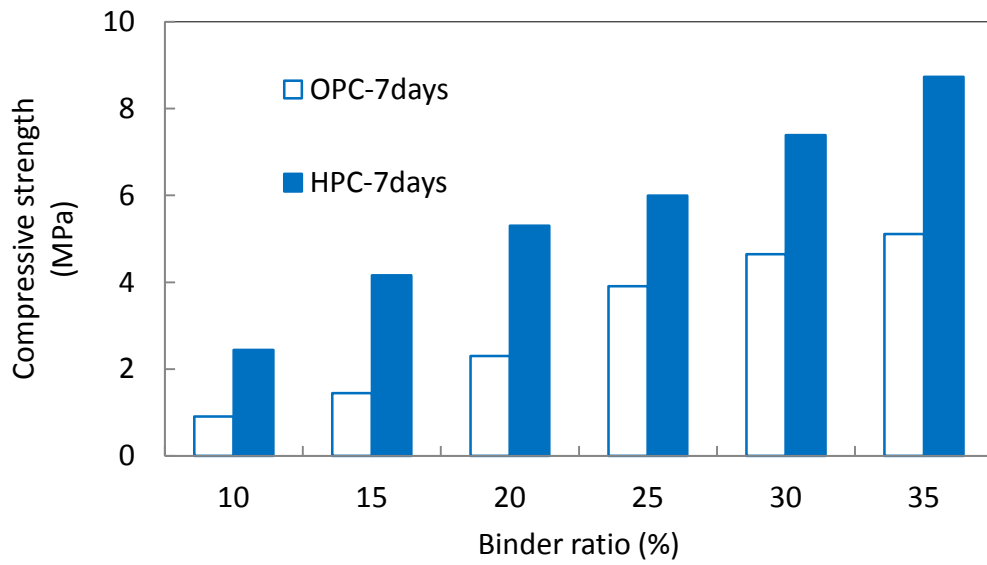


Fig. 4.13 Comparison of compressive strength between OPC and HPC for 7 days

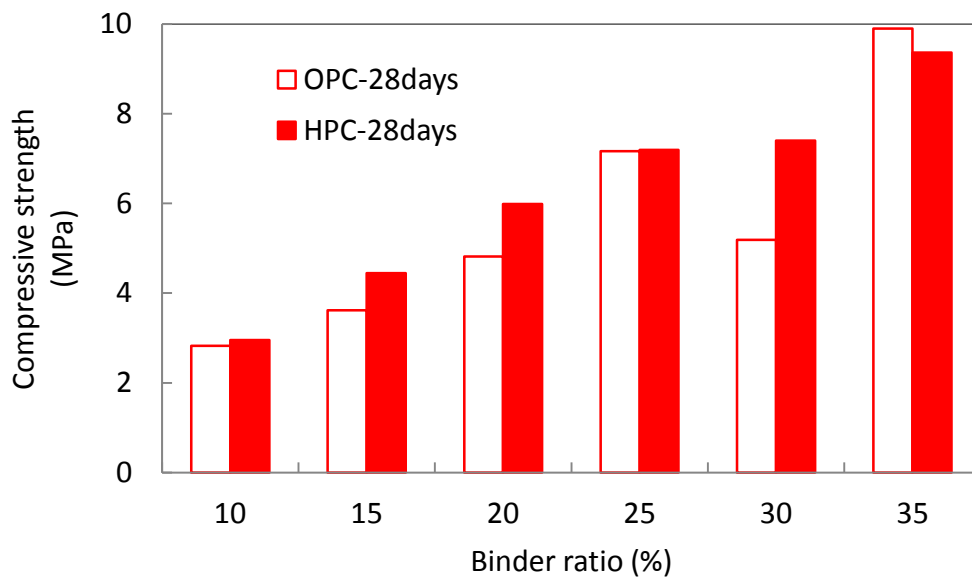


Fig. 4.14 Comparison of compressive strength between OPC and HPC for 28 days

In the case of 28 days, as shown in Fig. 4.14, both mortars made of HPC and OPC respectively, reach the target value of strength at the same binder ratio of 15%. The target value has reached much earlier and with lower binder ratio in case of HPC, which

is quite obvious because of its nature of hydration reaction.

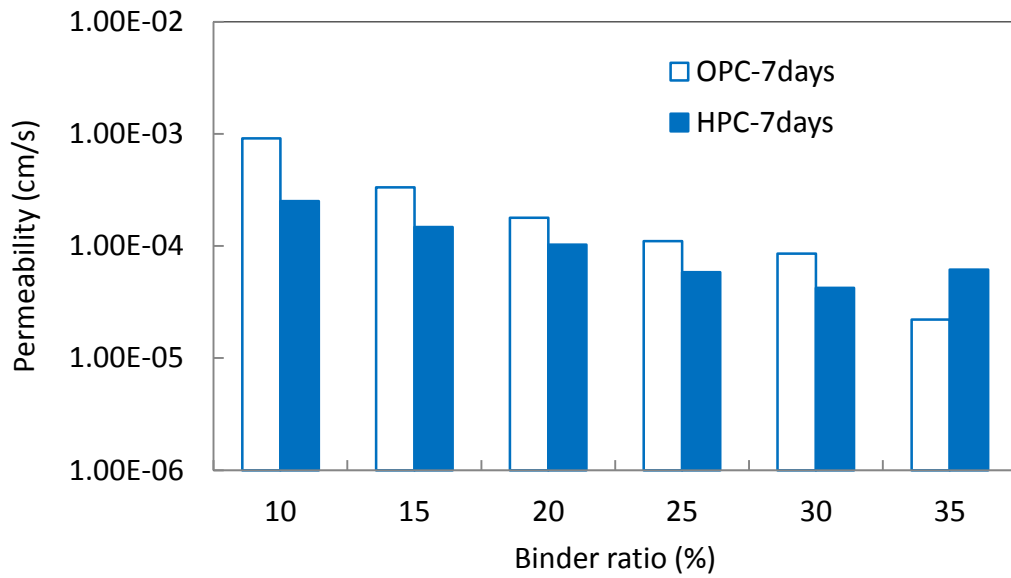


Fig. 4.15 Permeability comparison between OPC and HPC mortars after 7 days of curing.

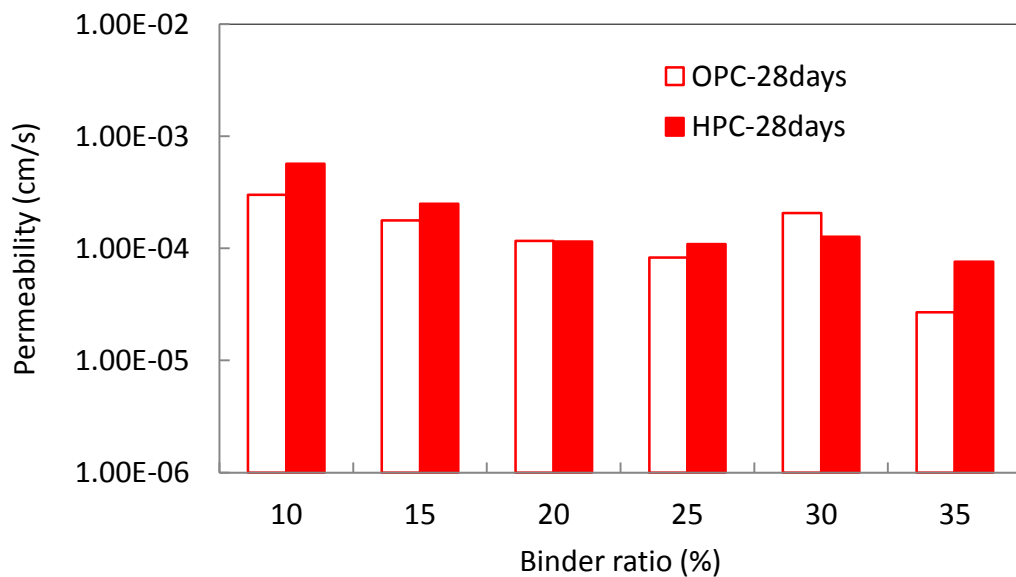


Fig. 4.16 Permeability comparison between OPC and HPC mortars for 28 days

Fig. 4.15 and Fig. 4.16 show comparison of permeability between both mortars using OPC and HPC, after 7 or 28 days of curing respectively. Permeability of mortar using HPC examined after 28 days curing seems to be the same or a little larger comparing with the one of OPC, while it is smaller in HPC mortar than in OPC one under 7days curing. Furthermore, regardless of cement type used, the permeability of the mortars with 15% or less of binder ratio can achieve the target value of  $5 \times 10^{-5}$  cm/s.

#### **4.1.8 Summary**

Permeable pavement technique with cement as binder and sand as fine aggregate are being practically used worldwide. For a good permeable pavement fairly good compressive strength and permeability are important factors. Higher compressive strengths lead to denser pavement rendering it impermeable.

An attempt to use both recycled waste like gypsum and Shirasu which is unused natural resource is tried in this study by suitably proportioning the materials in mortar to produce permeable pavements. Two types of Shirasu are used as fine aggregates having high water absorbing capacity and fine particle fraction. In the examination of mortars with variation in gypsum, it is clear that both strength and permeability of the mortar using gypsum and Shirasu reach their target value when gypsum/binder ratio is 15% or more. On the other hand, in the case of experimentation on mortars with variation in Shirasu ratio, both strength and permeability of the mortar reach their target value when Shirasu ratio is 75% or less. This allows incorporation of high amount of Shirasu in the mix. Koriyama Shirasu has lesser fine particle fraction. As the fine particle fraction

increases, the pozzolanic reactivity of Shirasu increases which consequently renders the mortar impermeable. Therefore, Koriyama Shirasu having lesser fine particles is expected to keep the permeability for longer duration. Even though Shirasu is expected to have long term pozzolanic reactivity, Shirasu as fine aggregate (highly porous) can sustain the permeability without making the pavement much denser.

Shirasu as fine aggregate in pavement can be an alternate to traditional pavement where sand is used and is expected to be as effective as traditional pavements. Shirasu develops long term strength sufficient for pavement and makes it permeable by its pore structure. From this experimental investigation, we can propose mix proportion and construction methods for permeable pavement using Shirasu and recycled gypsum.

## **4.2 Leaching of Hexavalent Chromium from Pavement Materials**

### **4.2.1 General**

The water-soluble compounds of chromium in cement are most relevant, specifically compounds of the form Cr (VI). Chromium in the cement can originate from:

- 1) Raw materials or fuel,
- 2) Magnesite-chrome kiln refractory brick, if used,
- 3) Wear metal from raw mill grinding process, if chromium alloys are used, and
- 4) Additions such as gypsum, pozzolans, ground granulated blast furnace slag, mineral components, and cement kiln dust.

Hexavalent chromium compounds include chromium trioxide, chromic acid, sodium chromate, sodium dichromate, potassium dichromate, ammonium dichromate, zinc chromate, calcium chromate, lead chromate, barium chromate, and strontium chromate. Compounds of hexavalent chromium are strong oxidizers and unstable. Its solubility in water is related to reported health risks. The environmental standards for hexavalent chromium in any environment is less than or equal to 0.05mg/l.

In the present study on permeable pavement, since gypsum and cement are used, there is a concern for leaching of hexavalent chromium. For permeable pavement, magnesium oxide (MgO) is also introduced as one of the binders. Therefore, leaching property of hexavalent chromium by cement, gypsum and MgO are studied using simple methods to analyze the amount of Cr(VI).



#### 4.2.2 Experimental Outline

Determination of hexavalent chromium leached from mortar with gypsum plasterboards and cement as binder is done by making paste with different mix proportions shown in Table 4.5. Here specimens are made by using both OPC and High Early Strength Portland cement (HPC) for comparison. Specimens are cast in moulds of diameter 5cm and length of 10cm.

Table 4.5 Mix proportion for testing each material for Cr(VI) (unit weight, kg/m<sup>3</sup>)

	W/B	W	B
OPC	50%	612	1223
HPC		610	1220
MgO		638	1277
Gypsum		555	1109

Table 4.6 and Table 4.7 show the mix proportions for paste with partial replacement of gypsum and also with both gypsum and MgO as binders respectively. In the mix proportion with replacement of gypsum (Table 4.6), two different replacement levels of gypsum with HPC and only 15% replacement of gypsum in OPC is done. In the mix proportion with gypsum and MgO as binders, HPC only is used with different percentages of gypsum and MgO in total binder content.

Table 4.6 Mix proportion for paste with replacement of gypsum in cement

Cement type	W/B	Gypsum/Binder	Unit weight (kg/m <sup>3</sup> )		
	(%)	(%)	Water	Cement	Gypsum
HPC15	56	15	630	949	167
HPC20	56	20	627	888	222
OPC15	36	15	525	1224	216

Table 4.7 Mix proportion for paste with replacement of gypsum and magnesium oxide in cement

	Cement type	W/B	MgO (M)	Gypsum (G)	Unit weight (kg/m <sup>3</sup> )			
		(%)	(%)	(%)	Water	Cement	M	G
HPC15-M5	HPC	56	5	15	629	909	45	168
HPC15-M10			10		630	869	87	169
HPC15-M15			15		630	832	125	169
HPC20-M5			5	20	625	851	43	223
HPC20-M10			10		627	814	81	224
HPC20-M15			15		627	779	117	224

Another set of mix proportions are made for paste with different kind of watering technique practiced for permeable pavements shown in 4.1.4 and 4.1.5. The mix proportion is given in Table 4.8. Pastes are made with the following mix proportions are cured under same technique for permeable pavement to simulate the actual condition.

Table 4.8 Mix proportion for paste with permeable pavement curing technique

Cement type	Gypsum/Binder (%)	Cement	Gypsum	Total weight (kg)
HPC	15	850	150	1000
	20	800	200	
OPC	15	850	150	

Determination of Cr(VI) from water leached out of permeable pavement mortar using Shirasu as fine aggregate is done using mix proportions shown in Table 4.9.

Table 4.9 Mix proportion for permeable pavement with Sand/Shirasu (kg)

Gypsum ratio (%)	HPC:MgO:Gypsum	Aggregate (Sand/Shirasu)	HPC	MgO	Gypsum	Total weight (kg)
15	85:00:15	800	170	0	30	1000
	81:04:15		162	9		
	76:09:15		153	17		
	72:13:15		145	26		
20	80:00:20		160	0	40	
	76:04:20		152	8		
	72:08:20		144	16		
	68:12:20		136	24		

Gypsum ratio in total binder content is kept at 15% and/or 20% and the ratio of HPC and MgO in binder is varied as shown in the table. Permeable pavements are made using the mix proportions for both sand and Shirasu as fine aggregate and the results are compared. Water that is leached out from permeable pavements made for permeability test is examined for hexavalent chromium content with the help of simple pack. At each interval of 30 minutes, water percolating thorough the specimen is collected and measured for Cr(VI) up to 2 hours.

#### **4.2.3 Determination of Hexavalent Chromium**

Determination of Cr(VI) is done using a simple pack as shown in Fig 4.17. It contains a chemical called diphenylcarbazide which changes color when reacts with soluble Cr(VI). The intensity of color depends on the concentration of Cr(VI) in the sample. The samples prepared for each mix proportion are cut and slices of 1cm thickness are removed at each curing period. Slices are then crushed and divided into 3 samples for analysis using simple pack. One gram each of powdered samples are mixed in water to make a solution of 100ml, filtered and the filtrate is used to measure Cr(VI). Simple pack containing diphenylcarbazide reacts with hexavalent chromium under acid conditions to form a red-violet color. Colorized sample is then matched with chart available in Simple Pack shown in Fig. 4.18. Results are expressed as ppm (mg/l) Cr(VI).



Fig. 4.17 Simple pack containing diphenylcarbazide

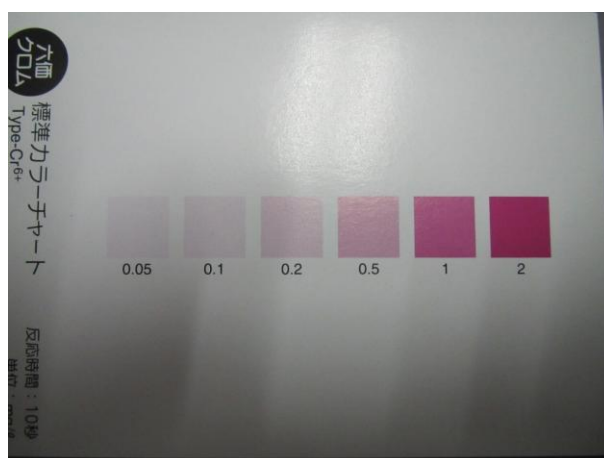


Fig. 4.18 Color chart for determination of Cr(VI) concentration (mg/l)

#### 4.2.4 Results and Discussion

The concentration of Cr(VI) in individual materials is shown in the tables below. Table 4.10 shows the amount of Cr(VI) in materials in original powder form (not mixed with water). The Cr(VI) concentration in the case of OPC is higher than HPC and Cr(VI) is not detected in gypsum and MgO powder. Therefore, it is confirmed that cement contains some amounts of hexavalent chromium.

Table 4.10 Concentration of Cr(VI) in original material in powder form

Hexavalent chromium detection result (powder)				
(mg/l)				
	Gypsum	MgO	HPC	OPC
1	0	0	0.05	0.2
2	0	0	0.1	0.1
3	0	0	0.05	0.1

The results for Cr(VI) with paste made of the same materials with mix proportion in Table 4.5 are shown in Table 4.11. From the results, there is significant content of Cr(VI) in OPC and HPC, but no Cr(VI) content in gypsum and MgO both for powder form and paste. When comparing with OPC and HPC, the content is almost same except for OPC at 3, 7 and 14 days of curing period where the content is more than environmental standards for health safety of 0.05mg/l. This confirms that there is slight content of Cr(VI) in both kinds of cement.

Table 4.11 Cr(VI) detection for respective pastes (mg/l)

Gypsum

	1 day	3 days	7 days	14 days	28 days
1	0	0	0	0	0
2	0	0	0	0	0
3	0	0	0	0	0

MgO

	1 day	3 days	7 days	14 days	28 days
1	0	0	0	0	0
2	0	0	0	0	0
3	0	0	0	0	0

OPC

	1 day	3 days	7 days	14 days	28 days
1	0.05	0.05	0.05	0.05	0.05
2	0.05	0.1	0.1	0.05	0.05
3	0.05	0.05	0.05	0.1	0.05

HPC

	1 day	3 days	7 days	14 days	28 days
1	0.05	0.05	0.05	0.05	0.05
2	0.05	0.05	0.05	0.05	0.05
3	0.05	0.05	0.05	0.05	0.05

### **Hexavalent chromium detection in case of paste with replacement of gypsum as binder**

The concentration of Cr(VI) for pastes with mix proportions shown in Table 4.6 are illustrated in Table 4.12. From the results it is observed that Cr(VI) crosses the prescribed limit in the case of HPC. However, in HPC 20, high concentration of hexavalent chromium occurs in some cases but not quite acceptable when considering health effects. OPC, when compared to HPC has higher content of Cr(VI) and crosses the limit of 0.05mg/l. The overall results show higher levels of Cr(VI) due to higher amounts of cement. Higher levels of gypsum replacement show less amount of Cr(VI) which means that the contribution to higher levels of Cr(VI) is due to cement.

Table 4.12 Cr(VI) detection in pastes with gypsum

#### **HPC15**

	3 days	7 days	14 days	28 days
1	0.1	0.1	0.1	0.1
2	0.1	0.1	0.2	0.1
3	0.05	0.1	0.1	0.1

#### **HPC20**

	3 days	7 days	14 days	28 days
1	0.1	0.05	0.05	0.1
2	0.05	0.05	0.1	0.05
3	0.05	0.1	0.1	0.1



### OPC15

	3 days	7 days	14 days	28 days
1	0.2	0.1	0.1	0.2
2	0.1	0.1	0.1	0.1
3	0.2	0.1	0.1	0.1

### Hexavalent chromium detection in case of paste with replacement of gypsum and MgO as binder

The following tables shows the amount of Cr(VI) in each mix proportions for pastes according to Table 4.7. From the result, it can be confirmed that as the replacement level of MgO increases, the overall content of Cr(VI) does not exceed 0.05mg/l. This is because the cement content in mix decreases as shown in mix proportions in Table 4.7.

Table 4.13 Cr(VI) detection in pastes with gypsum and MgO  
HPC20M5

	3 days	7 days	14 days	28 days
1	0.05	0.05	0.1	0.05
2	0.05	0.05	0.05	0.1
3	0.1	0.1	0.05	0.05

### HPC20M10

	3 days	7 days	14 days	28 days
1	0.05	0.1	0.05	0.05
2	0.05	0.05	0.05	0.05
3	0.05	0.05	0.05	0.1

### HPC20M15

	3 days	7 days	14 days	28 days
1	0.05	0.05	0.05	0.05
2	0.05	0.05	0.1	0.05
3	0.05	0.05	0.05	0.05

HPC15M5

	3 days	7 days	14 days	28 days
1	0.05	0.05	0.05	0.05
2	0.1	0.05	0.1	0.05
3	0.05	0.1	0.1	0.1

HPC15M10

	3 days	7 days	14 days	28 days
1	0.05	0.05	0.05	0.05
2	0.1	0.05	0.05	0.05
3	0.05	0.05	0.05	0.05

HPC15M15

	3 days	7 days	14 days	28 days
1	0.05	0.05	0.05	0.05
2	0.05	0.05	0.05	0.05
3	0.05	0.05	0.05	0.05

Also, MgO is thought to have inhibitory effect on hexavalent chromium and traps it from leaching. Even though there are some cases where Cr(VI) crosses limit, HPC 20 with any replacement has slight increase in Cr(VI) than the HPC 15.

#### **Hexavalent chromium detection in case of paste made by spraying technique**

To determine the Cr(VI) in permeable pavement, pastes with mix proportions shown in Table 4.8 are prepared and cured based on the techniques employed for permeable pavement. The permeable pavement curing technique is employed to analyze by simulating the actual condition in permeable pavement commercially in practice. The results obtained from the tests (Table 4.13) show that both HPC15 and HPC20 have higher concentrations of Cr(VI). This is because; the curing technique used for permeable pavement is different from normal mixing of water. The curing technique used for permeable pavement makes the matrix more permeable. Higher permeability of matrix leaches out chemicals very easily.

Table 4.14 Cr(VI) detection for paste with water spraying technique

HPC15

	3 days	7 days	14 days	28 days
1	0.1	0.1	0.05	0.1
2	0.05	0.1	0.05	0.1
3	0.1	0.2	0.1	0.05

HPC20

	3 days	7 days	14 days	28 days
1	0.1	0.1	0.1	0.1
2	0.1	0.1	0.05	0.05
3	0.1	0.1	0.1	0.1

**Hexavalent chromium detection for permeable pavement mortar with replacement of gypsum and MgO as binder along with HPC and Shirasu as fine aggregate**

**Compressive strength for permeable pavement**

The comparative compressive strength results for permeable pavement between sand and Shirasu as fine aggregates are shown in Fig. 4.19. The strength of Shirasu based permeable pavement is lesser compared to that of sand irrespective of gypsum replacement. Even though such a trend is seen, Shirasu based permeable pavement has required strength property for a good pavement by reaching the target value in almost all cases. Reduction in strength is due to higher volume of Shirasu used (mix proportion on weight basis) and that Shirasu itself is highly porous in nature. Permeable pavement

with sand and Shirasu has same binder paste volume. Therefore, paste volume available for coating higher volumes of Shirasu is insufficient.

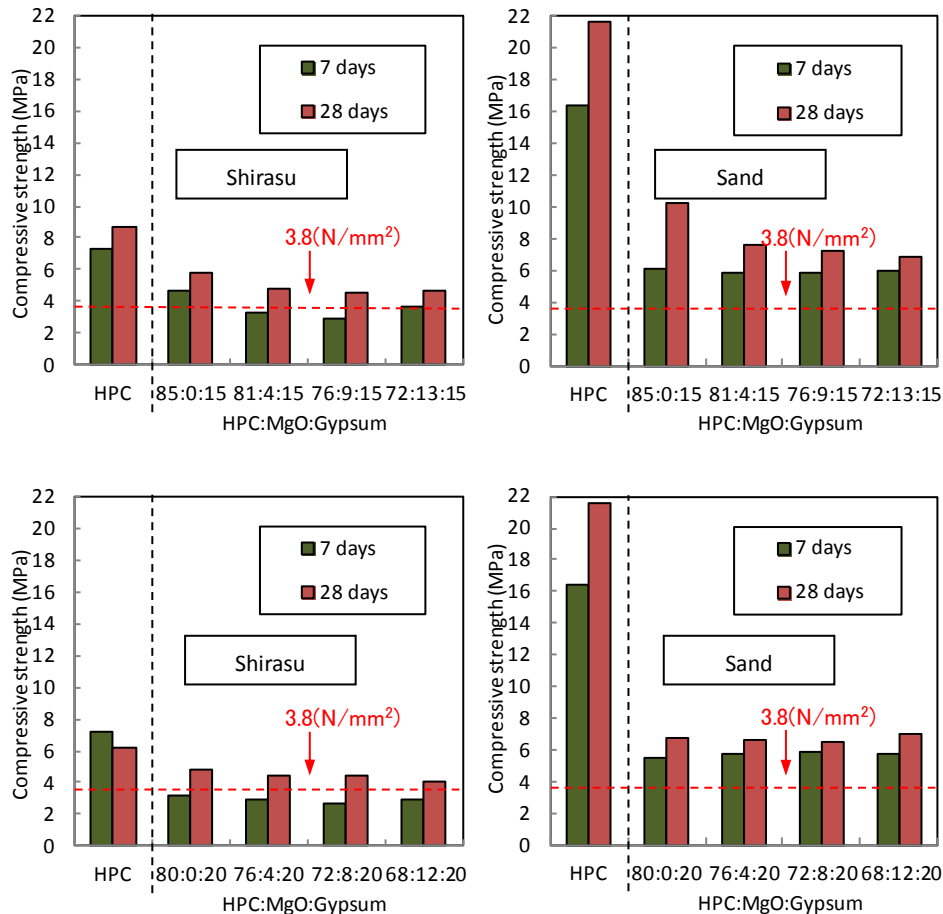


Fig. 4.19 Compressive strength results for permeable pavement with both sand and Shirasu

### Permeability of pavements

Fig. 4.20 shows the permeability results for permeable pavements made with sand and Shirasu. From the results, it is clear that permeability of Shirasu pavement where gypsum of 15% is used is slightly higher compared to the ones with sand. Also, in some cases, the permeability of Shirasu pavement where 20% gypsum is used is slightly higher or equal to that of sand. The results show that Shirasu, which is highly porous

contributes to higher permeability for pavements.

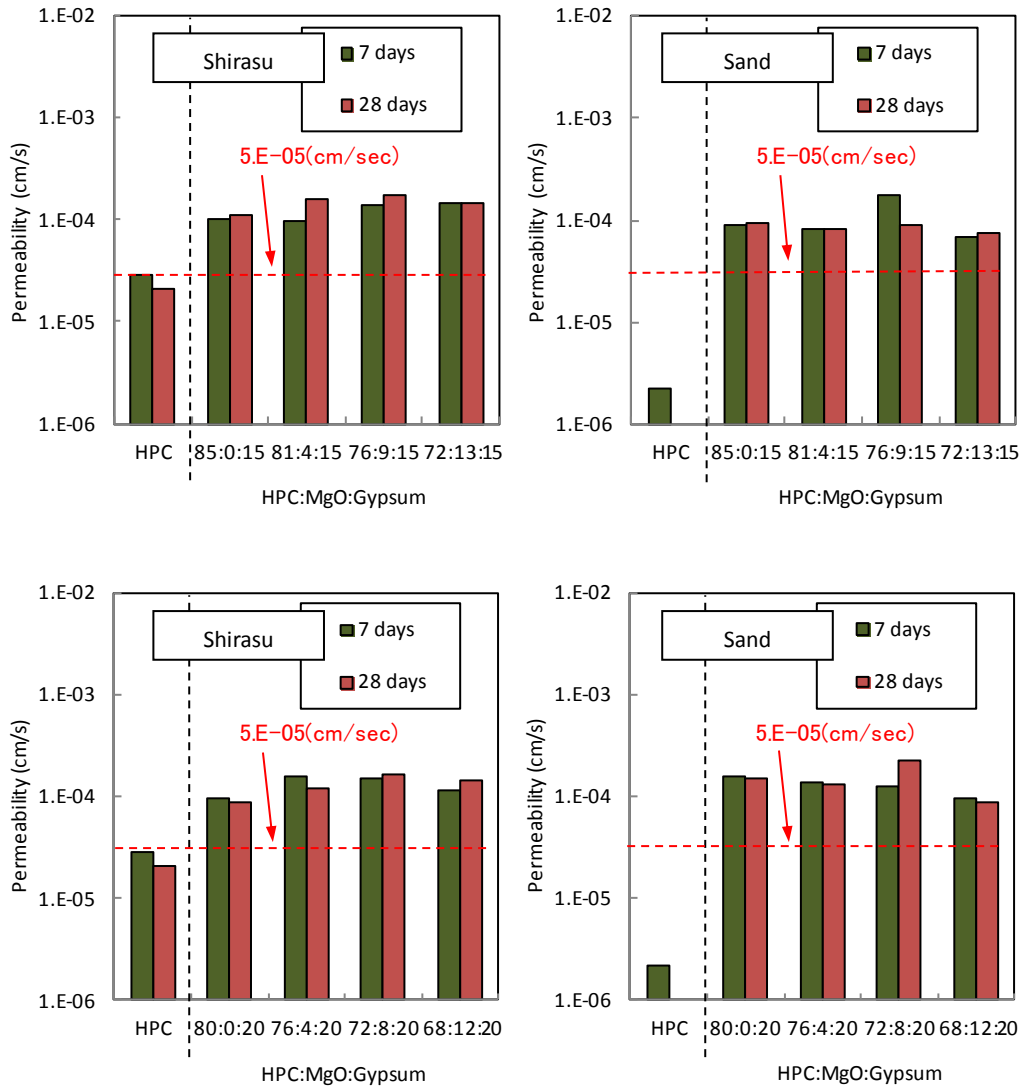


Fig. 4.20 Permeability results for permeable pavement with both sand and Shirasu

#### Hexavalent chromium with gypsum ratio of 15%:

Hexavalent chromium concentration after 7 days and 28 days of material age for both Shirasu and sand as fine aggregate with gypsum ratio of 15% are shown in Fig. 4.21 and Fig. 4.22. From the experimental results, Cr(VI) concentration is higher in case of

Shirasu as fine aggregate compared to mortar with sand as fine aggregate for both material ages of 7 days and 28 days.

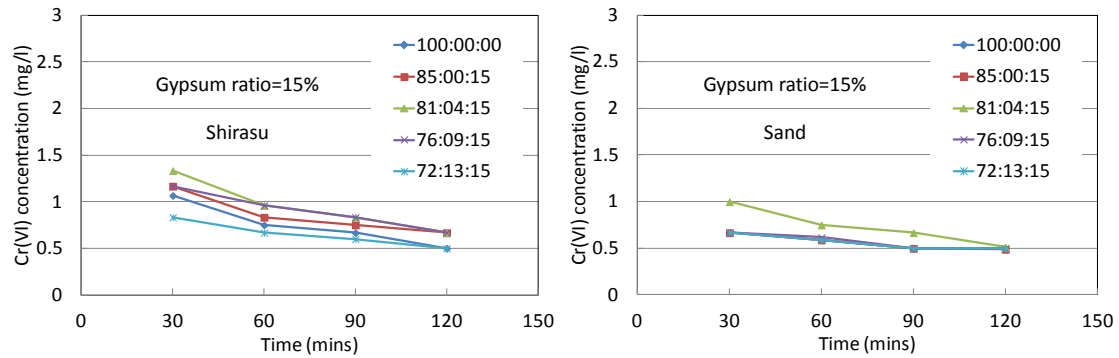


Fig. 4.21 Cr(VI) concentration at each 30min interval after 7 days of material age

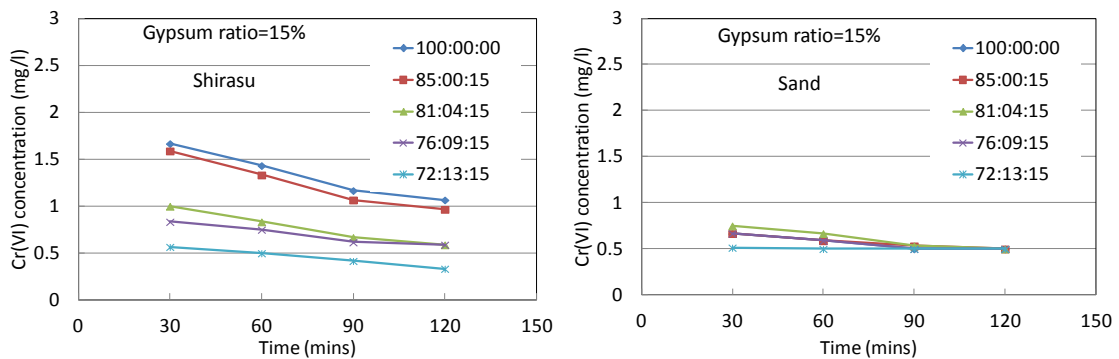


Fig. 4.22 Cr(VI) concentration at each 30min interval after 28 days of material age

Shirasu is highly porous in nature and hence the amount of Cr(VI) leaching is higher than sand. Especially in case of Shirasu, as the amount of MgO in the mix increases, concentration of Cr(VI) reduces. Previous results also showed that, increase in MgO reduces the concentration of Cr(VI) leaching out. MgO is believed to have inhibitory effect on Cr(VI) and trap the chromium from leaching. At the material age of 28days, Cr(VI) is lower in case of Shirasu than sand for higher amounts of MgO.

### Hexavalent chromium with gypsum ratio of 20%:

Hexavalent chromium concentration after 7 days and 28 days of material age for both Shirasu and Sand as fine aggregate with gypsum ratio of 20% are shown in Fig. 4.23 and Fig. 4.24. Concentration of Cr(VI) is higher in case of Gypsum ratio of 20% than in the case of 15% for mortar with Shirasu as fine aggregate. Also, the Cr(VI) concentration in the case of sand as fine aggregate is much lesser than Shirasu. Moreover, higher the amount of MgO, lower the concentration of Cr(VI).

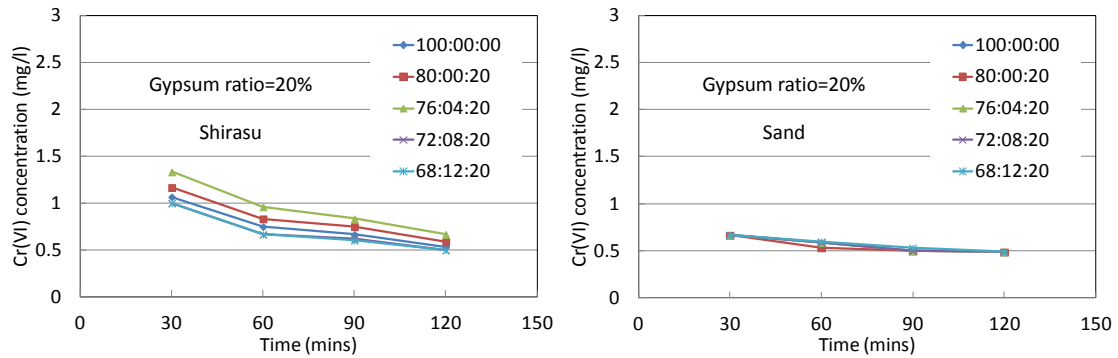


Fig. 4.23 Cr(VI) concentration at each 30min interval after 7 days of material age

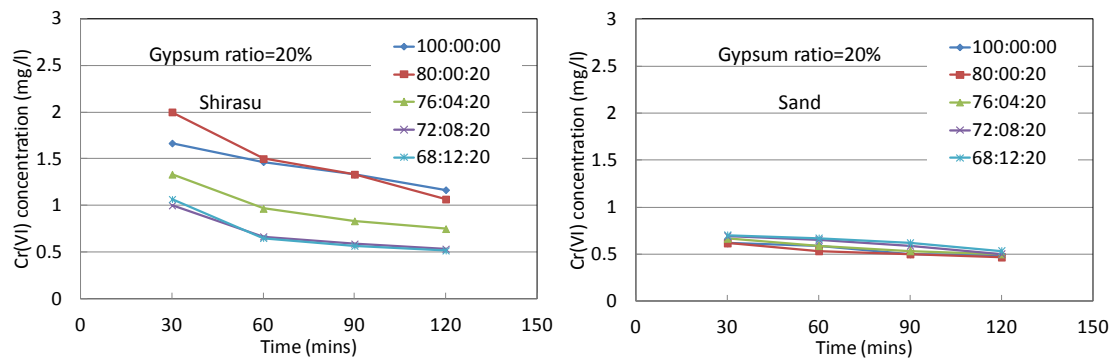


Fig. 4.24 Cr(VI) concentration at each 30min interval after 28 days of material age

### **Cumulative concentration of hexavalent chromium with gypsum ratio of 15%**

The total concentration of Cr(VI) is calculated from percolated water collected after the permeability test is done for the samples. Fig. 4.25 shows the cumulative concentration of Cr(VI) for different mix proportions of permeable pavement mortar in both cases where Shirasu or sand used as fine aggregate where gypsum ratio is kept at 15%. The Cr(VI) concentration is higher in case of Shirasu compared to that of sand. However, in some mix proportions with Shirasu where binder ratio is 72:13:15, the concentration level is almost same as sand. This confirms the ability of MgO to inhibit chromium by adsorption.

Cumulative concentration of Cr(VI) in the case of gypsum ratio at 20% is shown in Fig. 4.26. When comparing the concentrations of Cr(VI) based on gypsum ratio, as gypsum ratio increases the chromium reaching increases, which is not desired concerning the objective of study. As the MgO content in the mix increases the leaching reduces, clearly showing the effect of Cr(VI) immobilization by MgO. The main reason for leaching of chromium to be high in case of Shirasu is the reduction of alumina. Alumina is found in  $C_3A$  of cement and in Shirasu. Alumina is also known to immobilize chromium ions. Therefore, when gypsum is used as an admixture, alumina in both cement and Shirasu react with sulfates to form ettringite. This reduces the total amount of alumina and sulfate in the mix. Therefore, leaching of chromium is higher. Whereas, in case of sand, only alumina in  $C_3A$  forms ettringite with gypsum. Hence, lesser reduction of alumina than in case of Shirasu.



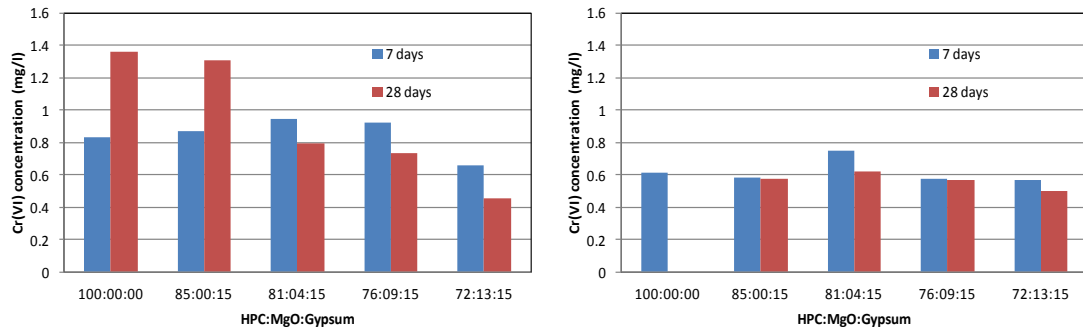


Fig. 4.25 Cumulative Cr(VI) concentration in case of gypsum ratio of 15%

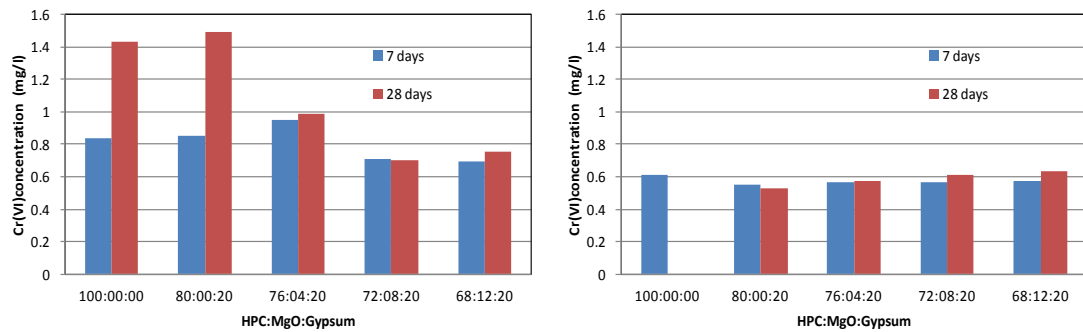


Fig. 4.26 Cumulative Cr(VI) concentration in case of gypsum ratio of 20%

## 4.2.5 Summary

Based on the findings and experimental results, cement used in permeable pavement material is confirmed to leach hexavalent chromium. The level of concentration of hexavalent is higher than environmental standards in many cases. Determination of hexavalent chromium leached by permeable pavement with Shirasu and/or sand as fine aggregate showed that, replacement of higher amounts of MgO reduces the leaching of chromium. MgO traps the chromium, inhibits and may immobilize chromium that prevents from leaching.

Shirasu as fine aggregate is observed to leach higher amounts of hexavalent chromium due to its porous nature. Permeable pavement with sand may have better packing effect without compromising the standards and requirements for good pavement. Partial replacement of cement by pozzolans or chemical admixtures like gypsum or magnesium oxide can solve the problem of leaching by hexavalent chromium inhibition. Replacement of MgO as binders can solve the problems encountered by using Shirasu. Therefore, permeable pavements can be effectively made by Shirasu as fine aggregate considering cement replacement materials like magnesium oxide and gypsum.

## **Chapter 5**

### **SHIRASU IN GEOPOLYMER**

#### **5.1 General**

Geopolymer has lately attracted considerable attention as one of the CO<sub>2</sub> free construction material, because of concrete free from any cementitious material. Alkali activated aluminosilicate source (pozzolans having high content of alumina and silica in their mineral composition) has proved to be strong and durable. These materials can exhibit wide range of applications and are highly resistive to chemical attack and fire. Study on geopolymer concrete using fly ash and metakaolin as aluminosilicate sources have been carried out in recent years. Fly ash geopolymer is observed to be much stronger and durable than Metakaolin based geopolymer. Fly ash based geopolymer concrete showed higher resistant to chemical attack and fire. Therefore, an attempt is made on studying strength characteristics of Shirasu based geopolymer mortar and compared to the fly ash based geopolymer with different mix proportions.

Geopolymer mortar is made with Shirasu as aluminosilicate source and mixture of sodium hydroxide solution and sodium silicate as alkaline activators. Three types of water to binder ratio, 40%, 50%, 60% are set. The specimens are subjected to different temperature conditions for heat curing and the performance of Shirasu geopolymer in terms of strength is analyzed and the strengths are also compared with geopolymer mortar with fly ash as aluminosilicate source and its variants. The parameters like

temperature and porosity, that influence the strength properties of geopolymer mortars are discussed and presented.

Silica and hydroxide balance in the mix proportion for geopolymer is considered to be one of the important parameters. Therefore, apart from mix proportions based on W/B alone, mix proportions based on silica to hydroxide ratio (“Si/OH”) is set for Shirasu and fly ash based geopolymer mortars and the properties of mortars are compared.

## **5.2 Mechanism of Geopolymerization**

The reaction of a solid aluminosilicate with a highly concentrated aqueous alkali hydroxide or silicate solution produces a synthetic alkali aluminosilicate material generically called a ‘geopolymer’, after Davidovits [5][6]. These materials can provide comparable performance to traditional cementitious binders in a range of applications, but with the added advantage of significantly reduced Greenhouse emission [7]. Depending on the raw material selection and processing conditions, geopolymers can exhibit a wide variety of properties and characteristics, including high compressive strength, low shrinkage, fast or slow setting, acid resistance, fire resistance and low thermal conductivity [8].

Materials generated by the alkaline activation of aluminosilicate sources have beneficial features, including rapid development of mechanical strength, fire resistance, dimensional stability, acid resistance, excellent adherence to aggregates and reinforcements. In the 1950s, Glukhovsky [9], proposed a general mechanism for the

alkali activation of materials primarily comprising silica and reactive alumina.

The Glukhovsky model divides the process into three stages:

- (a) destruction–coagulation;
- (b) coagulation–condensation;
- (c) condensation–crystallization.

Dissolution of the solid aluminosilicate source by alkaline hydrolysis (consuming water) produces aluminate and silicate species. Dissolution has always been assumed to be the mechanism responsible for conversion of the solid particles during geopolymerization. A complex mixture of silicate, aluminate and aluminosilicate species is thereby formed and the speciation equilibrium within these solutions occurs.

Dissolution of amorphous aluminosilicates is rapid at high pH, and this quickly creates a supersaturated aluminosilicate solution. In concentrated solutions this results in the formation of a gel, as the oligomers in the aqueous phase form large networks by condensation. This process releases the water that was nominally consumed during dissolution. As such, water plays the role of a reaction medium, but resides within pores in the gel. This type of gel structure is commonly referred to as bi-phasic, with the aluminosilicate binder and water forming the two phases.

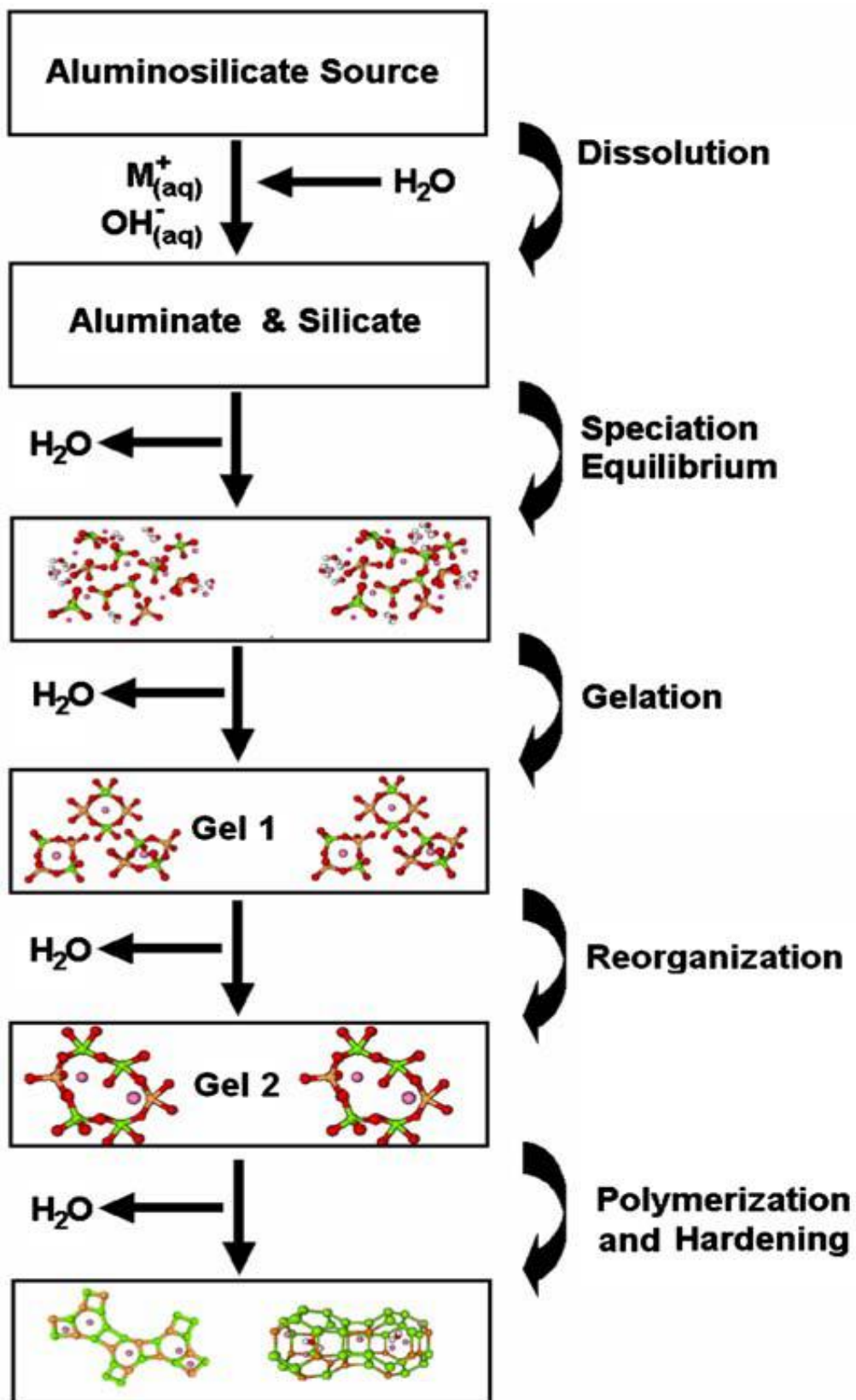
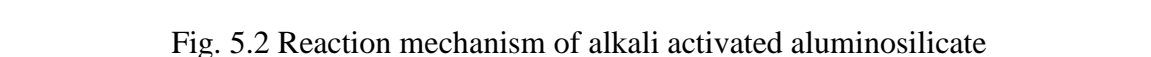


Fig. 5.1 Flowchart of geopolymerization process



Davidovits has also distinguished 3 types of polysialates depending on characteristics of silica and alumina in a specific pozzolan and their percentage.

1. Poly (sialate) type (-Si-O-Al-O),
2. Poly (sialate-siloxo) type (-Si-O-Al-O-Si-O) and
3. Poly (sialate-disiloxo) type (-Si-O-Al-O-Si-O-Si-O).

The structures of these polysialates can be schematized as in Fig. 5.3

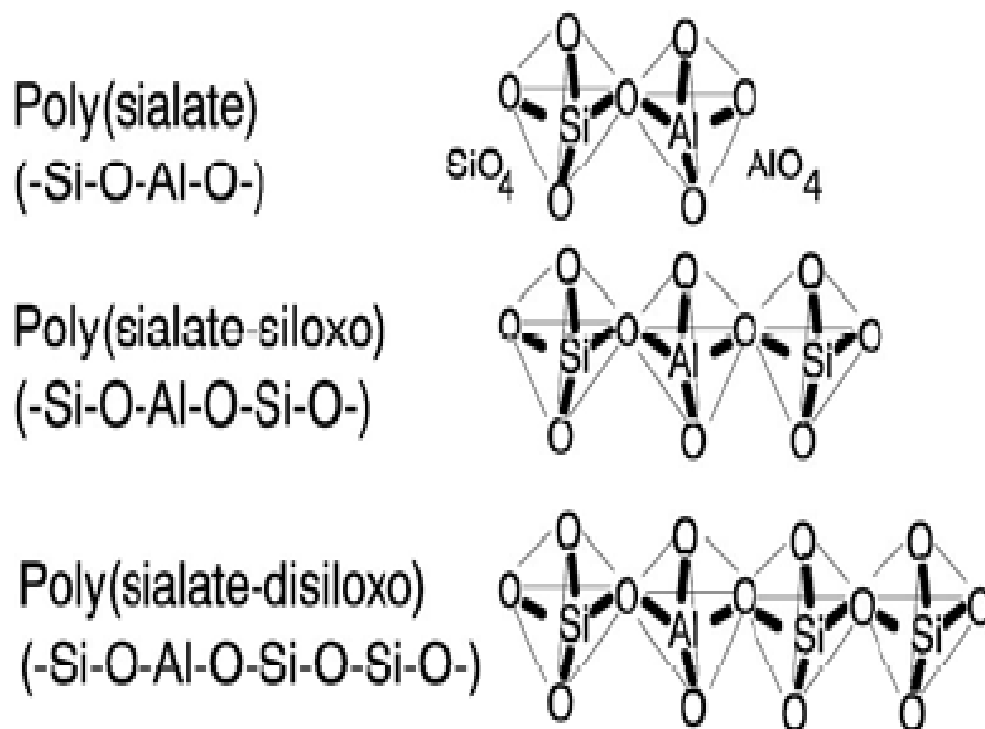


Fig. 5.3 Model of molecular structures of polysialates

The salient parameters affecting the compressive strength of geopolymer concrete are as listed below [10]:

1. Silicon oxide (SiO<sub>2</sub>)-to-aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) ratio by mass of the source



material; this ratio should preferably be in the range of 2.0 to 3.5 to make good concrete;

2. Activator liquids-to-source material ratio by mass;
3. Concentration of sodium hydroxide (NaOH) liquid measured in terms of Molarity (M), in the range of 8 to 14 M;
4. Sodium silicate-to-sodium hydroxide liquid ratio by mass; the effect of this parameter depends on the composition of the sodium silicate solution;
5. Curing temperature in the range of 60<sup>0</sup>C to 90<sup>0</sup>C;
6. Curing time.

### **5.3 Shirasu as Aluminosilicate Source**

Extensive research is carried out on geopolymer with fly ash. Shirasu also shows pozzolanic reactivity similar to fly ash and is characterized by high content of silica and alumina. Hence, potential of Shirasu needs to be exploited in geopolymer technology where Shirasu is used as aluminosilicate source. Shirasu, which is rich in silica and alumina, can play an important role as aluminosilicate source in geopolymer. Shirasu is confirmed to have pozzolanic reactivity and Shirasu concrete is being applied in various engineering constructions in recent years. Shirasu contains around 20% of very fine particles and is highly porous in nature. Past researches have proved that fly ash geopolymer are generally more strong and durable. With this knowledge, Shirasu is expected to perform similar to that of fly ash.

Three main types of geopolymer mortars are made, namely

1. Shirasu geopolymer (GSH): Shirasu as aluminosilicate source and river sand as aggregate.
2. Fly ash geopolymer (GFA): Fly ash as aluminosilicate source and river sand as aggregate.
3. Fly ash-Shirasu geopolymer (GFS): Fly ash as aluminosilicate source and Shirasu as aggregate.

The other types of geopolymer mortars are also made with volcanic ash and Shirasu balloon as aluminosilicate sources. The aluminosilicate sources are alkali activated with a mixture of sodium hydroxide and sodium silicate and heat cured under oven dry condition.

## **5.4 Materials**

Geopolymer mortar is made with following materials:

1. Aluminosilicate source (Binder): Shirasu having size under 75 $\mu$ m, fly ash, volcanic ash and Shirasu balloon.
2. Fine aggregate: River sand/Shirasu.
3. Alkaline activators: Sodium hydroxide (14N) and Sodium silicate (52% assay) are used under the condition of Sodium silicate/NaOH=2.5 by volume.

### **Characteristics of aluminosilicate sources**

The chemical and physical characteristics of all aluminosilicate sources used in the geopolymer mortar are shown in Table 5.1 and Table 5.2.

Table 5.1 Chemical characteristics of aluminosilicate sources used in geopolymer

Aluminosilicate source	Mass%						
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	MgO	Fe <sub>2</sub> O <sub>3</sub>
Fly ash	63.3	22.41	1.93	-	-	1.01	5.74
Shirasu	76.6	12.2	1.08	3.43	3.54	-	1.48
Shirasu Balloon	72.3	14.5	2	1.8	4.85	0.267	3.47
Volcanic Ash	53.7	16.6	10.3	1.82	1.8	1.59	11.9

Table 5.2 Physical characteristics of aluminosilicate sources used in geopolymer

Aluminosilicate source	Specific gravity	Water absorption
Fly ash	2.25	-
Shirasu	2.4	7.52%
Shirasu Balloon	2.1	16.43%
Volcanic Ash	2.69	-

Fly ash, Shirasu and Shirasu balloon have high amount of alumina and silica in their chemical composition. Volcanic ash has lesser silica and alumina content compared to other aluminosilicate sources.

Shirasu balloon is a processed form of Shirasu. Shirasu balloon particles are hollow glass microspheres which were first prepared by Dr Kimura using an electric furnace. It is manufactured by using a high-temperature fluidized sand-bed furnace that produces

Shirasu balloons with mean particle sizes of 40–1000 $\mu\text{m}$ . As the particles are spherical but hollow, water absorption of Shirasu balloon is two times than that of Shirasu (Table 5.2). Manufacture of Shirasu balloon using new technologies can produce particles of size of 20 $\mu\text{m}$ .

### 5.5 Mix Proportions

Table 5.3 and Table 5.4 show the mix proportions set for geopolymer mortars with Shirasu and fly ash as aluminosilicate sources, respectively. Water binder ratio (here-in-after called “W/B”) is set at 40%, 50% and 60%. Shirasu Geopolymer is named as “GSH” and fly ash Geopolymer as “GFA” in the present study. Geopolymer mortar with fly ash as aluminosilicate source and Shirasu as fine aggregate, named as “GFS” is also made and the mix proportion is given in Table 5.5. Shirasu used as fine aggregate for GFS mortar has a specific gravity of 2.15. The amount of alkaline activators in these three mix proportions are kept constant for better comparison of experimental results between geopolymers.

Table 5.3 Mix proportion for GSH ( $\text{kg/m}^3$ )

W/B	Shirasu	Sand	NaOH	$\text{Na}_2\text{SiO}_3$
40%	457	1655	78	176
50%	365	1756	78	176
60%	304	1823	78	176

Table 5.4 Mix proportion for GFA (kg/m<sup>3</sup>)

W/B	Fly ash	Sand	NaOH	Na <sub>2</sub> SiO <sub>3</sub>
40%	456	1624	78	176
50%	365	1729	78	176
60%	304	1803	78	176

Table 5.5 Mix proportion for GFS (kg/m<sup>3</sup>)

W/B	Fly ash	Shirasu	NaOH	Na <sub>2</sub> SiO <sub>3</sub>
40%	456	1322	78	176
50%	365	1408	78	176
60%	304	1468	78	176

### **Silica to hydroxide ratio (Si/OH)**

Based on the assumption that Si/OH in the mix design is one of the factors affecting the strength of mortars, Si/OH of GSH and GFA are varied from 6 to 12. The mix proportions based on Si/OH in GSH and GFA are shown in Table 5.6 and Table 5.7 respectively. The compressive strength tests are carried out for both GSH and GFA mortars heat cured at 90<sup>0</sup>C. The parameters affecting compressive strength are discussed and Si/OH in the mix is focused upon. Si/OH was calculated as follows:

1.  $Si = (\text{Silica in Shirasu/fly ash}) + (\text{Silica in Na}_2\text{SiO}_3)$
2.  $OH = \text{NaOH solution.}$

$$\frac{\text{Si}}{\text{OH}} = \frac{(\text{Silica in Shirasu/Flyash}) + (\text{Silica in Na}_2\text{SiO}_3)}{\text{NaOH}}$$

Table 5.6 Mix proportion based on Si/OH for GSH (kg/m<sup>3</sup>)

Si/OH	Shirasu	Sand	NaOH	Na <sub>2</sub> SiO <sub>3</sub>
12	401	1716	78	177
10	354	1716	87	195
9	326	1716	92	207
8	295	1716	97	219
6	221	1716	110	249

Table 5.7 Mix proportion based on Si/OH for GFA (kg/m<sup>3</sup>)

Si/OH	Fly ash	Sand	NaOH	Na <sub>2</sub> SiO <sub>3</sub>
12	414	1716	71	160
10	369	1716	80	179
9	343	1716	85	191
8	313	1716	90	204
7	278	1716	97	218

Mix proportions for Shirasu geopolymer with change in aggregate (sand) to Shirasu ratio (here-in-after called “Sand/Shirasu”) keeping Si/OH=9 as constant is done. Sand to Shirasu ratio is fixed at 3, 4 and 5 and the mix proportion is shown in Table 5.8. here, as the ratio changes the paste volume in the mixture also changes. But in the case of Table 5.6 and Table 5.7, paste volume is kept constant (because amount of sand is kept constant).

Table 5.8 Mix proportion with varying sand/Shirasu for Si/OH=9 for GSH (kg/m<sup>3</sup>)

Si/OH	Sand/Shirasu	Shirasu	Sand	NaOH	Na <sub>2</sub> SiO <sub>3</sub>
9	5	337	1686	95	213
	4	386	1546	109	245
	3	452	1360	127	286

Geopolymer mortar is also made with volcanic ash and Shirasu balloon as aluminosilicate source based on W/B.

Table 5.9 Mix proportion for GVA (kg/m<sup>3</sup>)

W/B	Volcanic ash	Sand	NaOH	Na <sub>2</sub> SiO <sub>3</sub>
40%	458	1707	78	176
50%	366	1797	78	176
60%	305	1857	78	176

Table 5.10 Mix proportion for GSHB (kg/m<sup>3</sup>)

W/B	Shirasu balloon	Sand	NaOH	Na <sub>2</sub> SiO <sub>3</sub>
40%	457	1584	78	176
50%	366	1698	78	176
60%	304	1777	78	176

The mix proportions of volcanic ash geopolymer (GVA) and Shirasu balloon geopolymer (GSHB) are shown in Table 5.9 and Table 5.10. Alkaline activators in these mix proportions are kept constant similar to the ones shown in Clause 5.5.

## 5.6 Curing Condition

Cylindrical specimens of diameter 5cm and length 10cm are casted and subjected to temperatures of 80<sup>0</sup>C and 90<sup>0</sup>C, in oven dry condition for all mix proportions.

## 5.7 Results and Discussion

### Shirasu geopolymer (GSH)

Geopolymer mortar with Shirasu of size under 75 $\mu$ m as aluminosilicate source is made with mix proportions given in Table 5.3. W/B is kept at 40%, 50% and 60%, and the specimens are cured under the conditions with 90<sup>0</sup>C and 80<sup>0</sup>C temperatures.

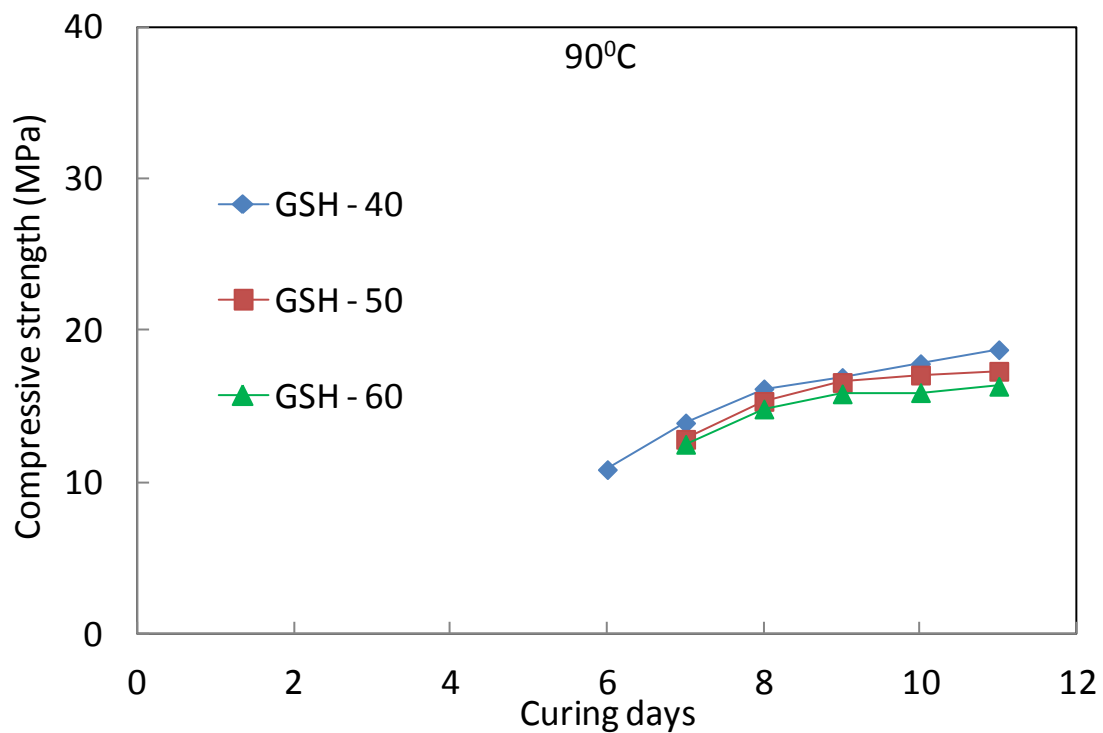


Fig. 5.4 Compressive strength variation with age



Then, compressive strength test is carried out for specimens for each set of mix proportions. The compressive strengths of specimens both at 90<sup>0</sup>C and 80<sup>0</sup>C are shown in Fig. 5.4 and Fig. 5.5 respectively. (For example GSH-40 means Shirasu geopolymer with W/B=40%).

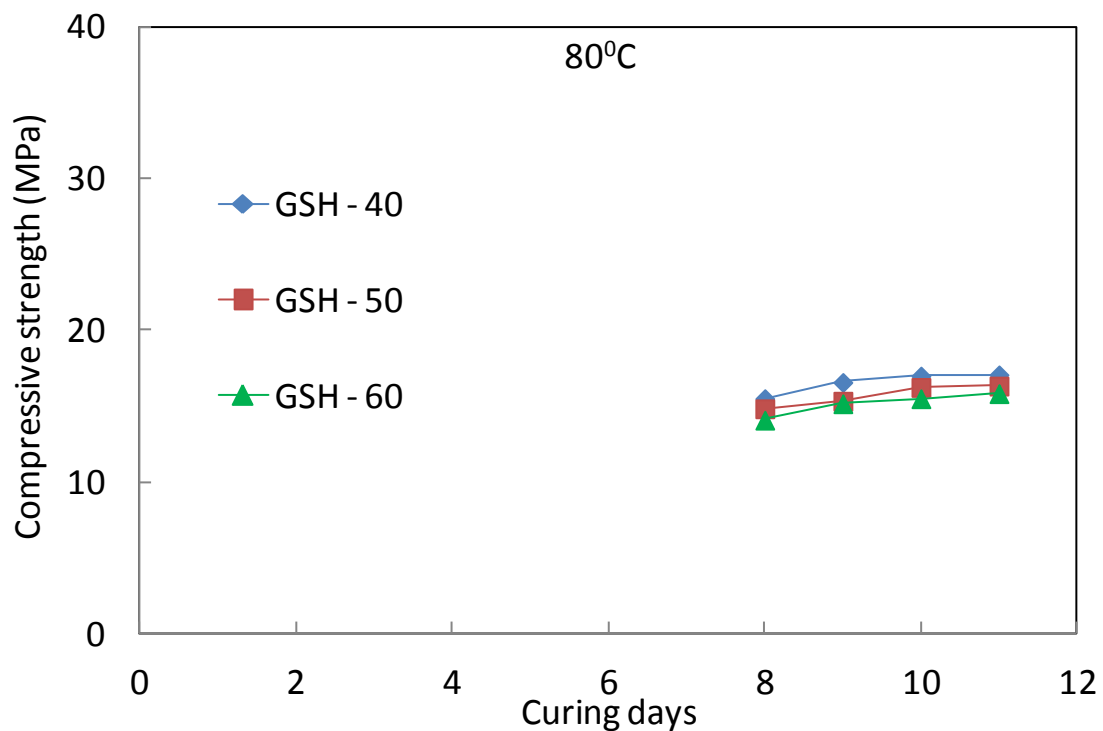


Fig. 5.5 Compressive strength variation with age

From the experimental results it is observed that at all ages of curing, there is not much change in compressive strengths for both temperature cases, although the compressive strength is higher in case of 90<sup>0</sup>C. This shows that the rate of polymerization depends on the temperature at which the specimen is cured. However, the strength develops only after 6 days in case of 90<sup>0</sup>C and 8 days in case of 80<sup>0</sup>C. This may be attributed to the fact that Shirasu has been deposited over thousands of years. Hence, impurities and

oxides coating on the surface of particles reduces the rate of polymerization and delays initiation of hardening. Even though such case arises, Shirasu clearly shows good performance in polymerization and the maximum compressive strength is up to 20MPa. Also, as W/B increases, the strength seems to decrease in both cases of temperatures. Consequently, W/B=40% has got the highest compressive strength compared to W/B=50% and W/B=60%.

### **Fly ash geopolymer (GFA)**

Fly ash geopolymer mortar is prepared with mix proportion as shown in Table 5.4. The amount of alkaline activators is kept same as that of Shirasu geopolymer to study the relative performance of Shirasu polymerization when compared to fly ash. The compressive strengths of fly ash geopolymers for both 90<sup>0</sup>C and 80<sup>0</sup>C are given in Fig. 5.6 and Fig. 5.7 respectively. Increase in W/B, shows increase in strength, unlike Shirasu geopolymer. This may be because of higher demand of alkaline activators in case of fly ash as it contains less amount of silica compared to Shirasu. However, strength change due to temperature is similar to the Shirasu geopolymer. Increase in temperature, increases the strength of mortar. Maximum strength of around 35MPa is achieved at W/B of 50% and 60% for 90<sup>0</sup>C curing. The maximum strengths in W/B=40% at 90<sup>0</sup>C and all W/B at 80<sup>0</sup>C are almost same as Shirasu geopolymer. The only major difference between Shirasu and fly ash geopolymer is that the fly ash Geopolymer gains strength after 1 day of curing, whereas strength development of Shirasu geopolymer is after 6 days. The contrast in result is the affect of the nature of Shirasu and fly ash. Even if both are pozzolans and have similar characteristics, Shirasu is a deposit and fly ash is a by-product.

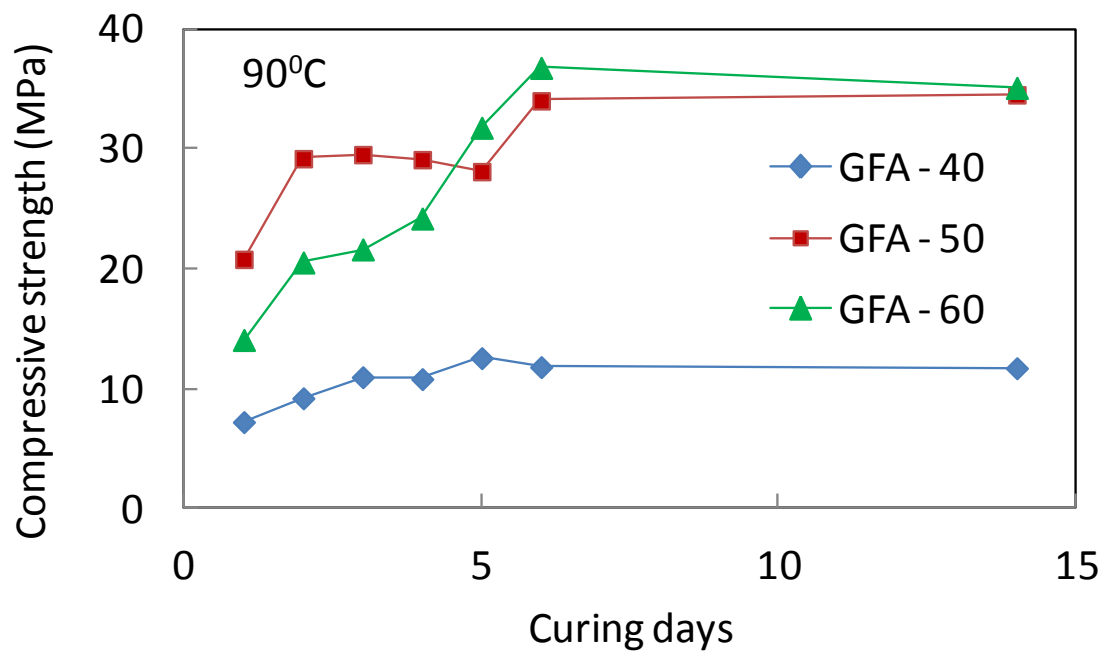


Fig. 5.6 Compressive strength variation with age

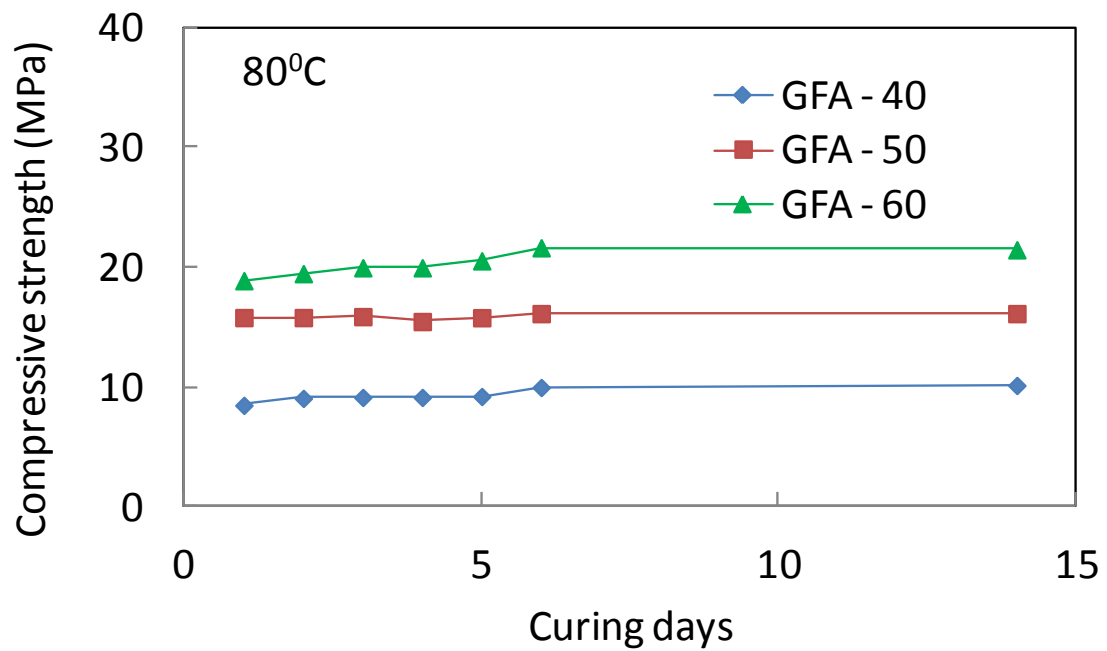


Fig. 5.7 Compressive strength variation with age

Shirasu was deposited several thousand years ago and has been subjected to various natural conditions which change the particle surface nature. The demand for sufficient alkali may not have been met in these mix designs. Also, silica content in both Shirasu and fly ash are different. Hence, for same amount of alkaline activators for Shirasu and fly ash based geopolymer, availability of silica in the mix differ in both case. This results in variation of compressive strength results. Overall results show that Shirasu can be potentially used in geopolymer.

#### **Geopolymer with fly ash as aluminosilicate source and Shirasu as aggregate (GFS)**

Geopolymer mortar with fly ash as aluminosilicate source and Shirasu as fine aggregate is made with mix proportions shown in Table 5.5. The compressive strength results for specimens subjected to 90<sup>0</sup>C and 80<sup>0</sup>C are shown in Fig. 5.8 and Fig. 5.9 respectively. In the case of GFS, the strength variation with W/B is similar to GFA where, increase in W/B increases the compressive strength for both temperature conditions. But the overall strength is much less and only reaches a maximum value of 9MPa for W/B=60% for 90<sup>0</sup>C. This is because the Shirasu which is used as fine aggregate is itself porous in nature. Silica content in the total mix is too high in the presence of both fly ash and Shirasu and sufficient alkaline activators are not available for polymerization.

The strength decreases as the temperature of curing decreases. Even though the strength has drastically reduced, the GFS mortar hardens after one day curing similar to GFA. This shows that fly ash as aluminosilicate has higher reactivity than Shirasu in polymerization reaction.

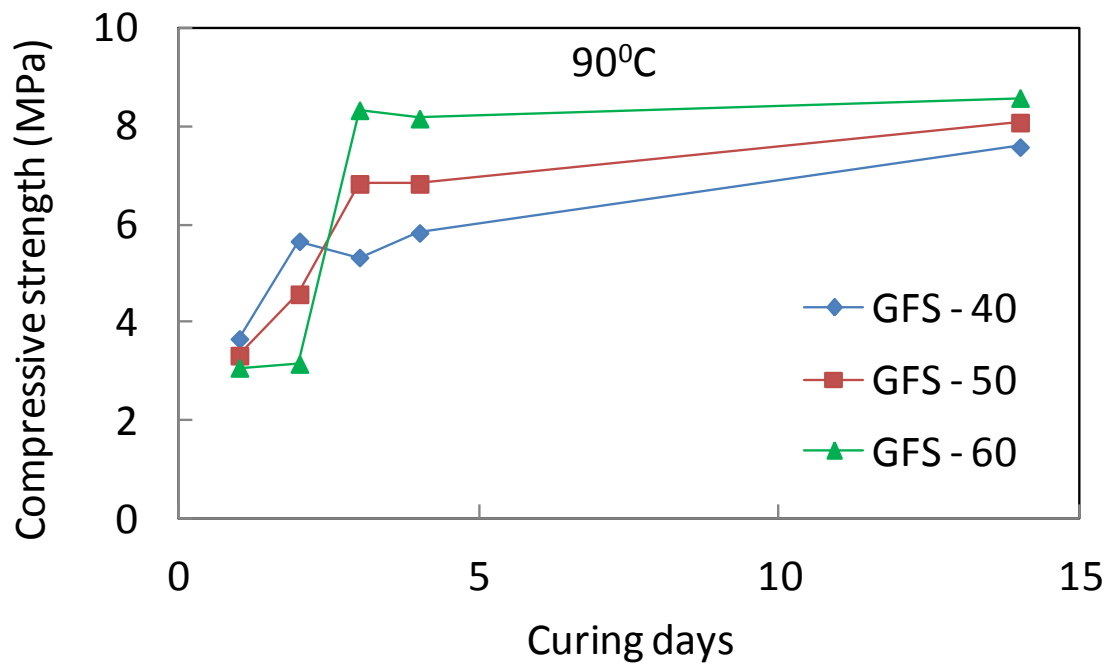


Fig. 5.8 Compressive strength variation with age

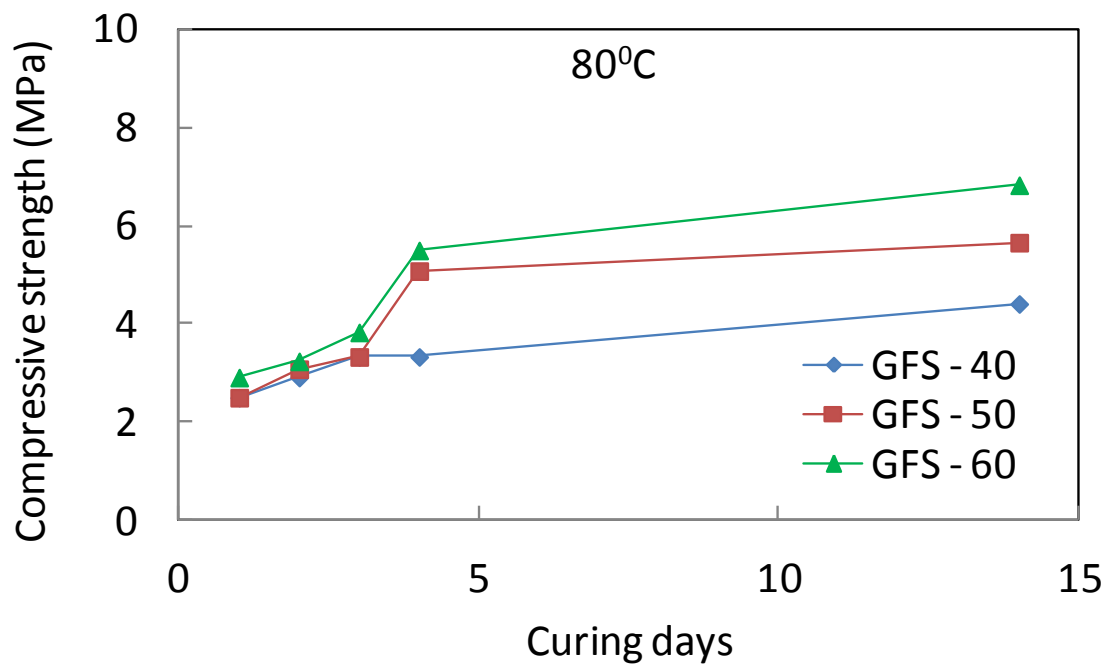


Fig. 5.9 Compressive strength variation with age

Shirasu used as fine aggregate in fly ash-Shirasu geopolymer is itself porous in nature and less dense than sand. The mortar becomes more light and porous and the strength decrease. This phenomenon is considered to be the initial physical effect. Secondly, in the study on different geopolymer mortars with mix proportions varying water to binder ratio, the alkaline activator is kept constant for all mortars for good comparison of strength development. Therefore, fly ash as binder in fly ash-Shirasu geopolymer has much higher reactivity and consumes all the alkaline activators to form polymer chain. Even though Shirasu is aluminosilicate source, it is used as fine aggregate and has much lesser reactivity. Only the fine particle fraction of about 20% may take part in reaction, but at a very slow rate. The total silica in the mix is too high with both fly ash and Shirasu. Therefore, the silica to hydroxide balance in the mix is not met and is too high. These combinations of factors lead to lesser gain in strength.

### **Porosity of geopolymer mortars**

Porosity of GSH, GFA and GFS subjected to 90<sup>0</sup>C for 7 days was determined for clear understanding of the variation in strengths. The relation of pore volume with pore size is given in Fig. 5.10. GSH mortars have highest volume of pores at 100µm and above. On the other hand, GFA-40 has high volume of pores at 100µm, GFA-50 at 1µm and GFA-60 at 10nm. GFS mortars have high volume of pores at size range of 10µm to 100µm.

The cumulative pore volume distribution for all mortars cured at 90<sup>0</sup>C for 7 days is shown in Fig. 5.11 shows. Total pore volume is highest in the case of GFS and lowest for GFA. The total pore volume is in the order of GFA<GSH<GFS.

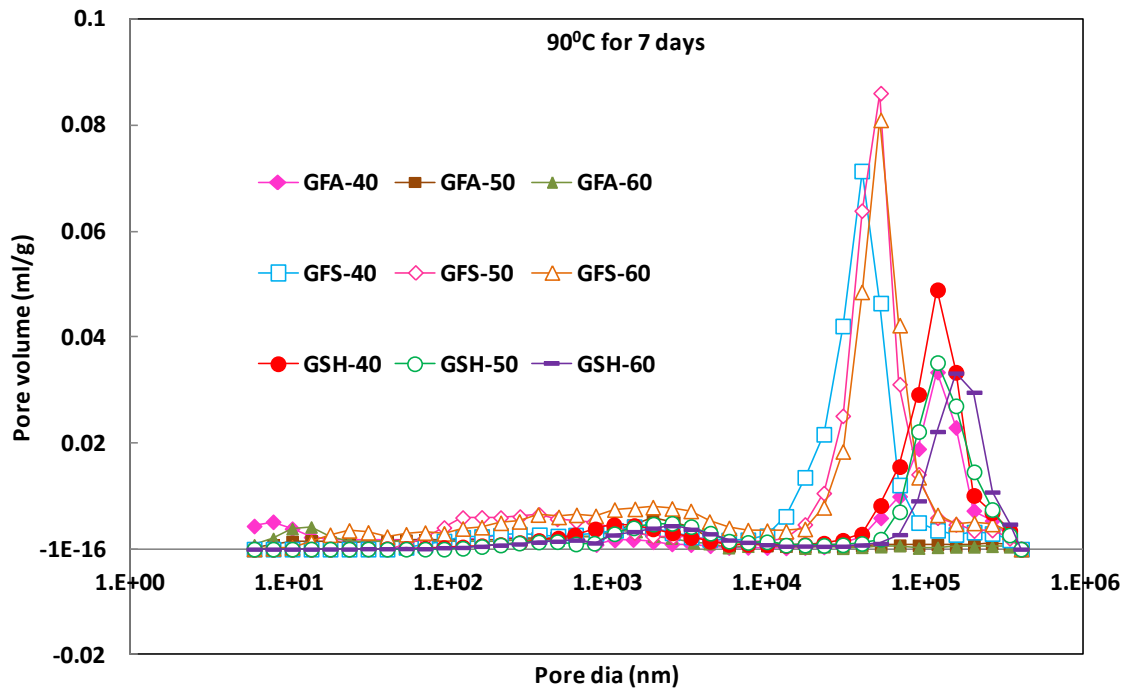


Fig. 5.10 Pore volume distribution for all specimens subjected to temperature of 90°C for 7 days

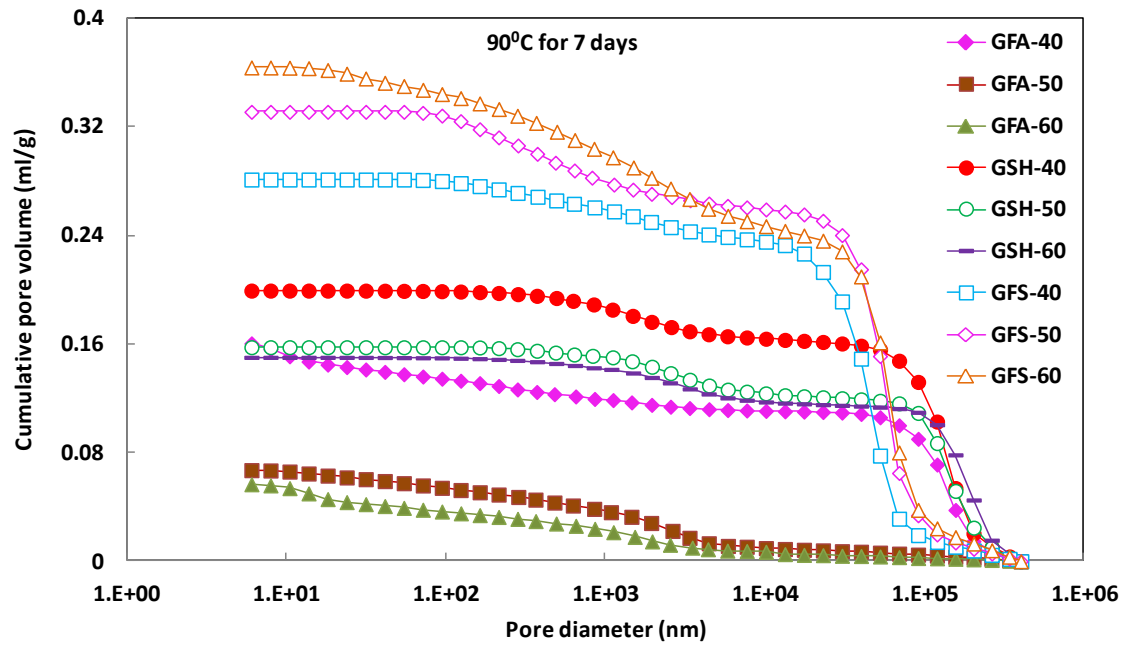


Fig. 5.11 Cumulative pore volume distribution for all mortars cured at 90°C for 7 days

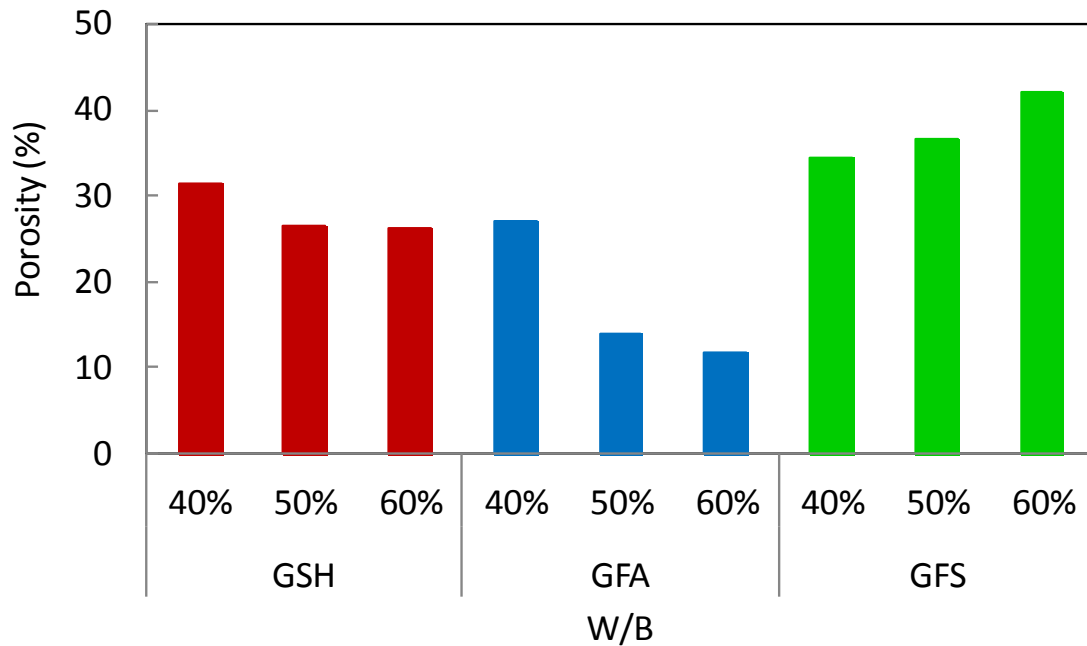


Fig. 5.12 Porosity of all mortars cured at 90°C for 7 days

The porosity results (Fig. 5.12) shows that GFA with W/B=60% has lowest porosity and GFA of W/B= 60% has highest porosity and the results match with the compressive strengths of each geopolymer mortars with different W/B. This trend in porosity of mortars indicates that porosity is one of the factors that affect the strength of these mortars. The pore volumes in each W/B for GSH and GFA explain the contrasting results of strength.

#### **Geopolymer mortar with acid treated Shirasu as fine aggregate and Fly ash as aluminosilicate source**

GFS mortars where Shirasu is used as fine aggregate has very less compressive strength when compared to other geopolymer mortars. Also, the porosity of GFS mortars is very high. This is due to the fact that Shirasu is highly porous in nature and the mortar



contains very high amount of Shirasu as it is used as fine aggregate. Second reason for low strength is that, Shirasu particles are weak in dissolution process during polymerization reaction.

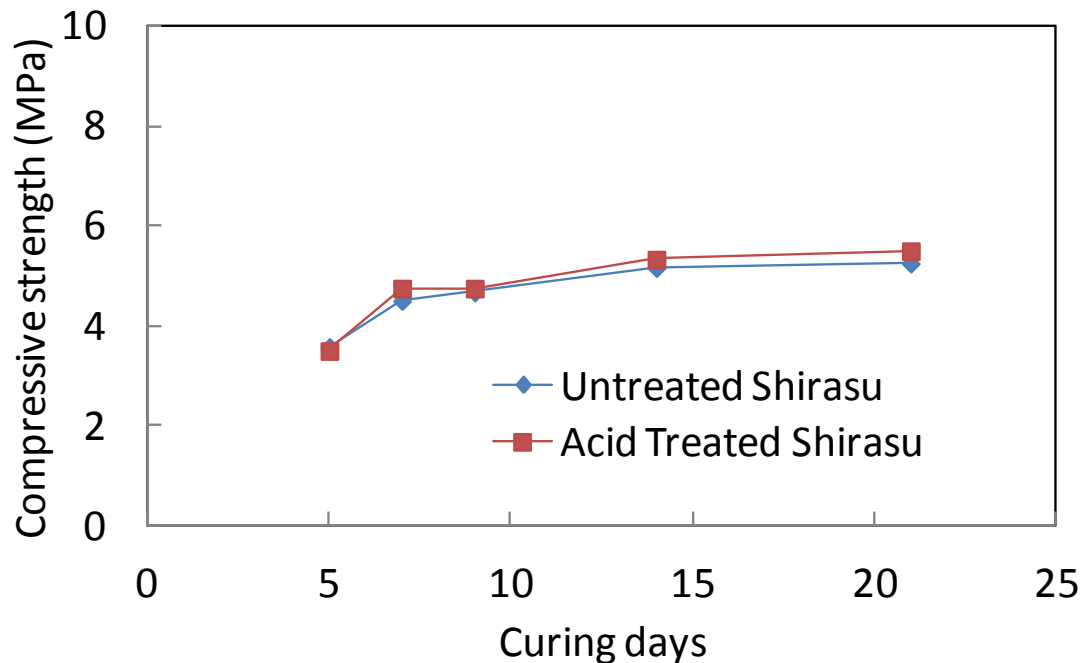


Fig. 5.13 Compressive strength comparison between untreated and acid treated Shirasu aggregate based geopolymer

Shirasu was deposited thousands of years ago and has undergone several changes in environmental conditions, temperature and pressure over the deposit. As it is a natural deposit and may contain impurities including some oxides, the particles may not be highly reactive at times. Therefore an attempt is made in treating Shirasu and removing the impurities to some extent. Shirasu is treated with hydrochloric acid of pH=3 and then used as aggregate in making geopolymer mortars. Shirasu is treated with acid for 24 hours. After acid treatment, Shirasu is washed completely in distilled water before

using it as aggregate. Mix proportion for geopolymer mortar is the same as the mix proportions for GFS mortar and mortar only with W/B=40% is prepared. GFS mortar with treated Shirasu is heat cured at 90<sup>0</sup>C. The compressive strength of GFS mortar and GFS mortar with treated Shirasu is compared and the results are shown in Fig. 5.13. The compressive strength for specimen with acid treated Shirasu is slightly higher when compared to normal Shirasu. Further treatment of Shirasu for longer duration or under stronger acids may probably show better strength than untreated Shirasu.

#### **Silica to hydroxide ratio (Si/OH)**

Silica and hydroxide balance in the mix is analyzed for its effect on strength development by testing the specimens prepared according to the mix proportions given in Table 5.6 and Table 5.7 for GSH and GFA respectively. The compressive strength results of GSH and GFA mortars heat cured at 90<sup>0</sup>C are shown in Fig. 5.14 and Fig. 5.15 respectively. The graphs illustrating the compressive strength depending on Si/OH shows clearly that Si/OH has a great influence on the strength properties of mortar. The peak compressive strength is obtained at Si/OH=9 for both Shirasu and fly ash based geopolymer mortars. This indicates a clear effect of silica to hydroxide balance in the mix.

The condition of Si/OH<9 has fewer amount of aluminosilicate source necessary for polymerization. On the contrary, the condition of Si/OH>9 has higher amount of alkaline activators in the mix which does not have enough aluminosilicate source necessary for polymerization. Higher amount of alkaline activators also increase the cost of preparation of mortars or concrete.

Compressive strength comparison between GSH at 13 days (highest compressive strength) and GFA at 7 days (highest compressive strength) with Si/OH is shown in Fig. 5.16. The peak compressive strength is obtained at Si/OH=9. Hence, Si/OH is an important parameter for development of strength irrespective of aluminosilicate sources used and their physical and chemical characteristics. But, the early hardening property or reactivity of pozzolans may not be improved only by Si/OH. Low reactivity in case of Shirasu geopolymer may be due to lesser amorphousness of Shirasu.

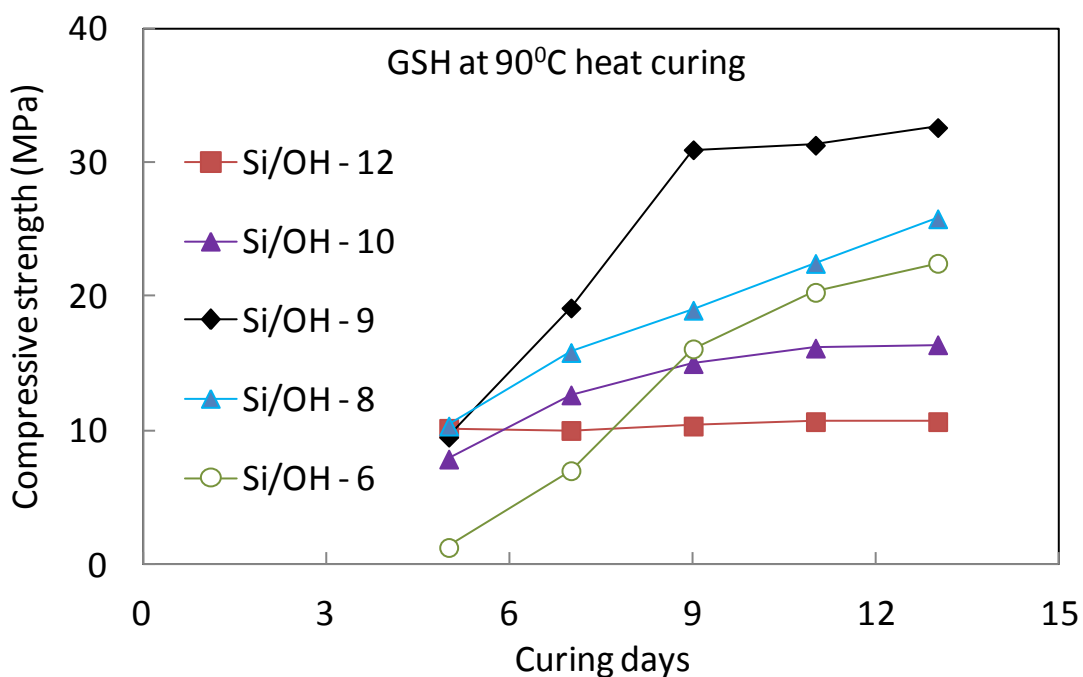


Fig. 5.14 Compressive strength for different Si/OH for Shirasu geopolymer

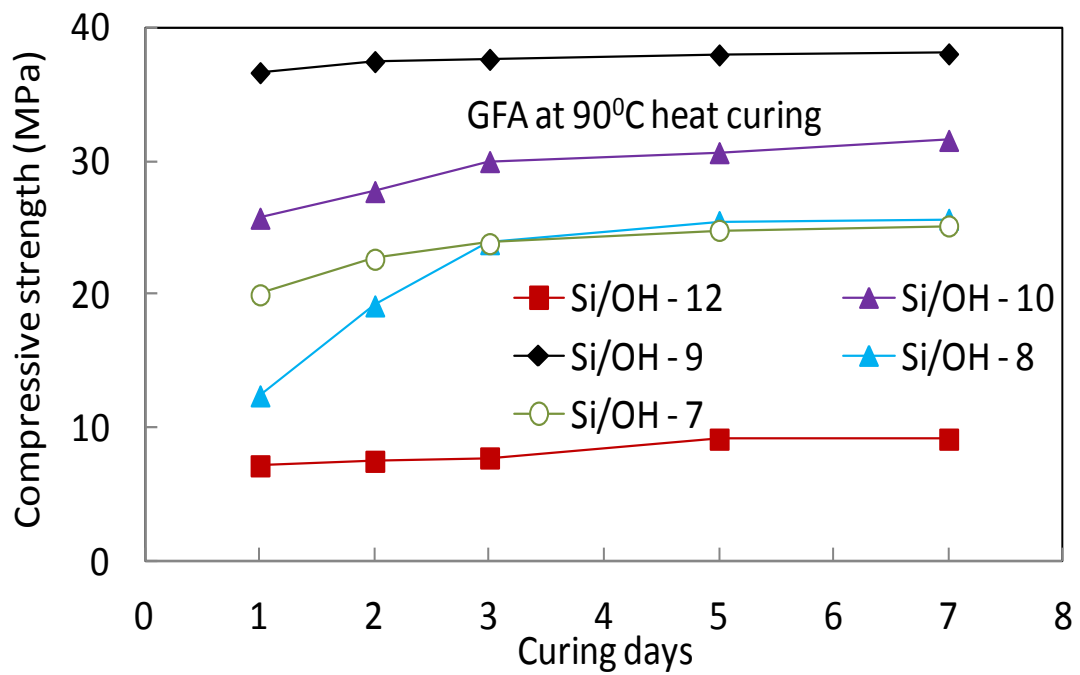


Fig. 5.15 Compressive strength for different Si/OH for fly ash geopolymer

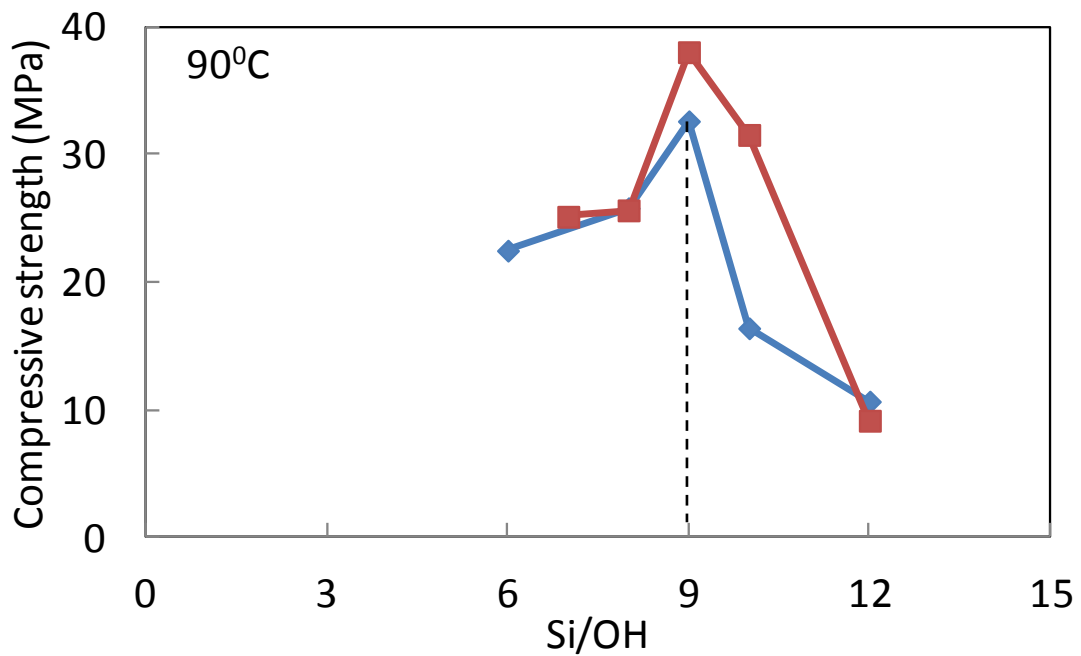


Fig. 5.16 Compressive strength versus Si/OH

Compressive strength results for Shirasu geopolymer with varying aggregate to Shirasu ratio keeping Si/OH constant at 9 (mix proportion in Table 5.8) is shown in Fig. 5.17. For example, “Si/OH – 9 – 5” means Si/OH=9 and sand to Shirasu ratio is 5. From the results, at early ages of heat curing, there is not much different between strengths of different aggregate to Shirasu ratio. At longer durations of heat curing the strength difference becomes larger. As the aggregate to Shirasu ratio decreases, there is slight increase in compressive strength at all ages of heat curing.

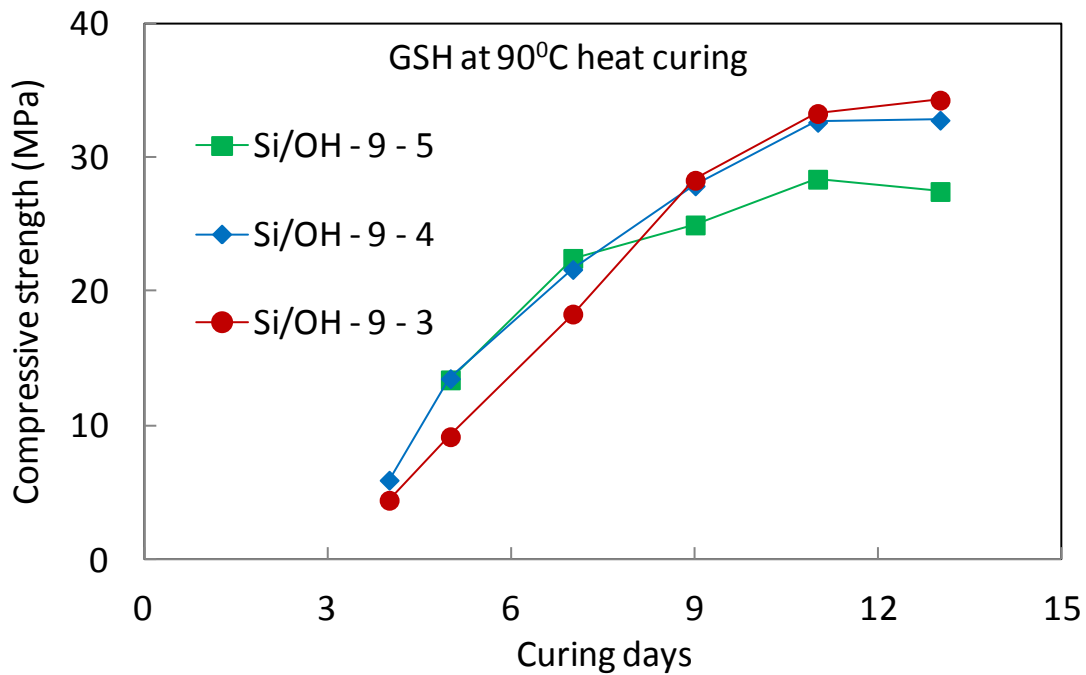


Fig. 5.17 Compressive strength for GSH of Si/OH=9 with change in aggregate to Shirasu ratio

This is due to the fact that, paste volume (amount of Shirasu and alkali) increases as the Sand/Shirasu decreases. This means higher amount of absolute aluminosilicate and alkali which results in more polymer reactions. Also as the paste volume increases, the

casting of specimens becomes easier due to high flow characteristics of fresh mortar. Especially, in the case of lower Sand/Shirasu, the reactivity is observed to be higher. The mortars harden after 4 days of heat curing. Previous results of strength based on W/B and Si/OH showed that the Shirasu geopolymer mortars harden after 6 days and 5 days respectively. Therefore, the effect of Si/OH and Sand/Shirasu in mix proportions on the strength development is confirmed.

### **Porosity of geopolymer mortars based on Si/OH**

The pore volume distribution for GSH and GFA mortars with mix proportions based on silica to hydroxide ratio heat cured at 90<sup>0</sup>C for 7 days is shown in Fig. 5.18. The pore volume has clearly reduced in the case of Si/OH when compared to the geopolymer mortars with mix proportions based only on W/B (Fig. 5.10). But, similar to Fig. 5.10, the pore volume for GSH mortar is high for pore size in the range of 100µm. This shows that Shirasu geopolymer has large sized pores in the matrix.

The cumulative pore volume distribution for GSH and GFA mortars with mix proportions based on silica to hydroxide ratio heat cured at 90<sup>0</sup>C for 7 days is shown in Fig. 5.19. Total pore volume in case of Shirasu geopolymer is higher than fly ash geopolymer. But, the difference in cumulative pore volume is lesser in the case of mortars with mix proportions based on Si/OH.

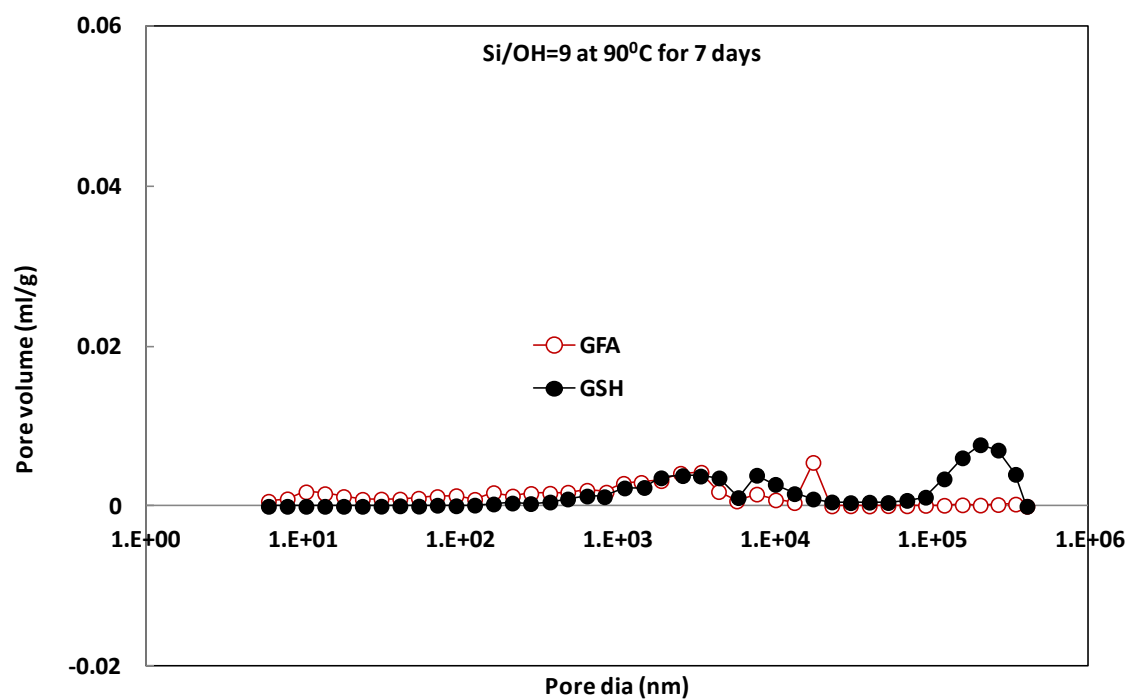


Fig. 5.18 Pore volume distribution for GSH and GFA based on Si/OH

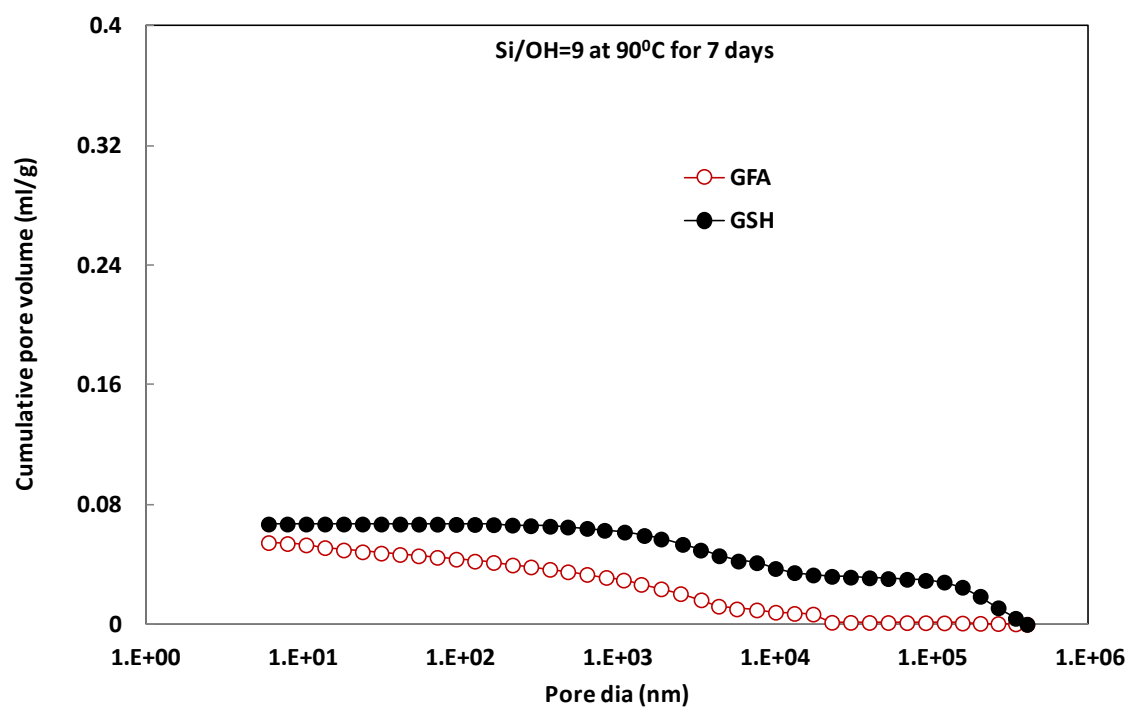


Fig. 5.19 Cumulative pore volume distribution for GSH and GFA based on Si/OH

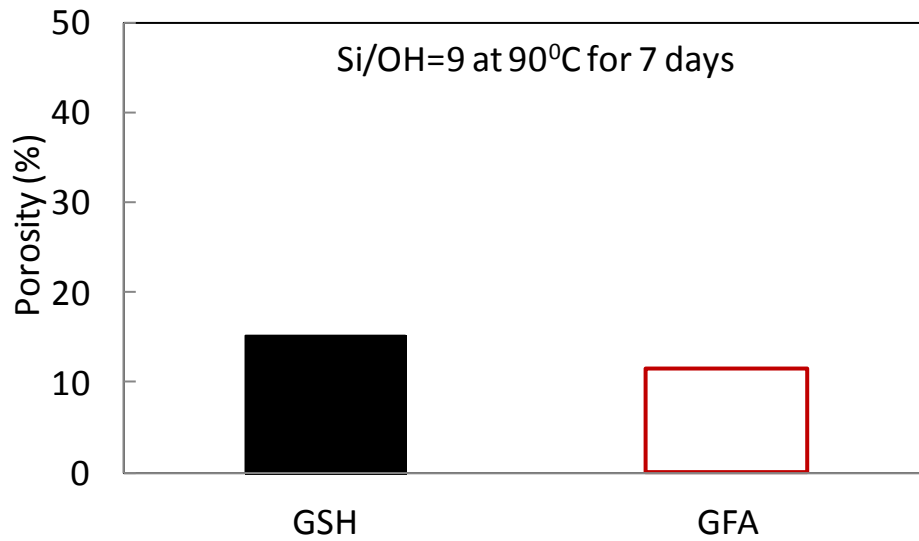


Fig. 5.20 Porosity of GSH and GFA based on Si/OH cured at 90<sup>0</sup>C for 7 days

The porosity of both GSH and GFA mortars are illustrated in Fig. 5.20. The porosity of geopolymer mortars based on Si/OH are significantly lesser compared to geopolymer mortars with mix proportions based on W/B (when compared with Fig. 5.12). Also, porosity of GFA much lesser compared to GSH.

#### **Volcanic ash geopolymer (GVA)**

Mortar specimens are made with volcanic ash as binder and sand as aggregate with mix proportions shown in Table 5.8. The specific gravity of volcanic ash is 2.69. The results for both temperatures of 90<sup>0</sup>C and 80<sup>0</sup>C are shown in Fig. 5.21 and Fig. 5.22 respectively. The mortar develops to gain strength only after 10 days of exposure which is economically not feasible even though the strength is as high as 20MPa. Volcanic ash is characterized by relatively low silica and alumina compared to other pozzolans and contains higher amount of impurities.



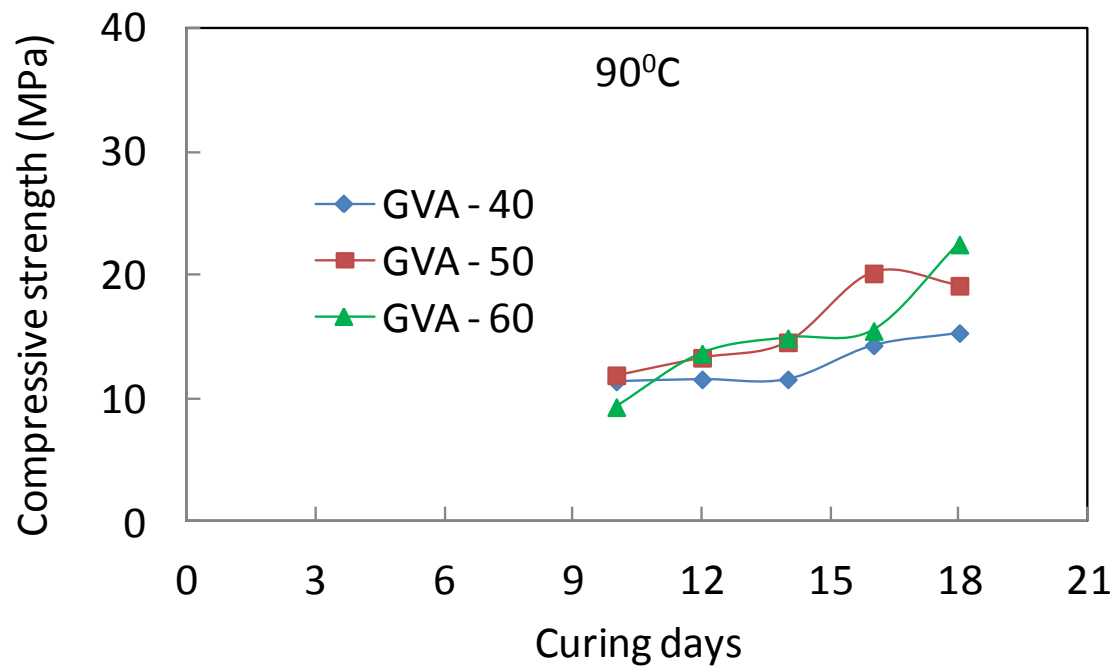


Fig. 5.21 Compressive strength variation with age

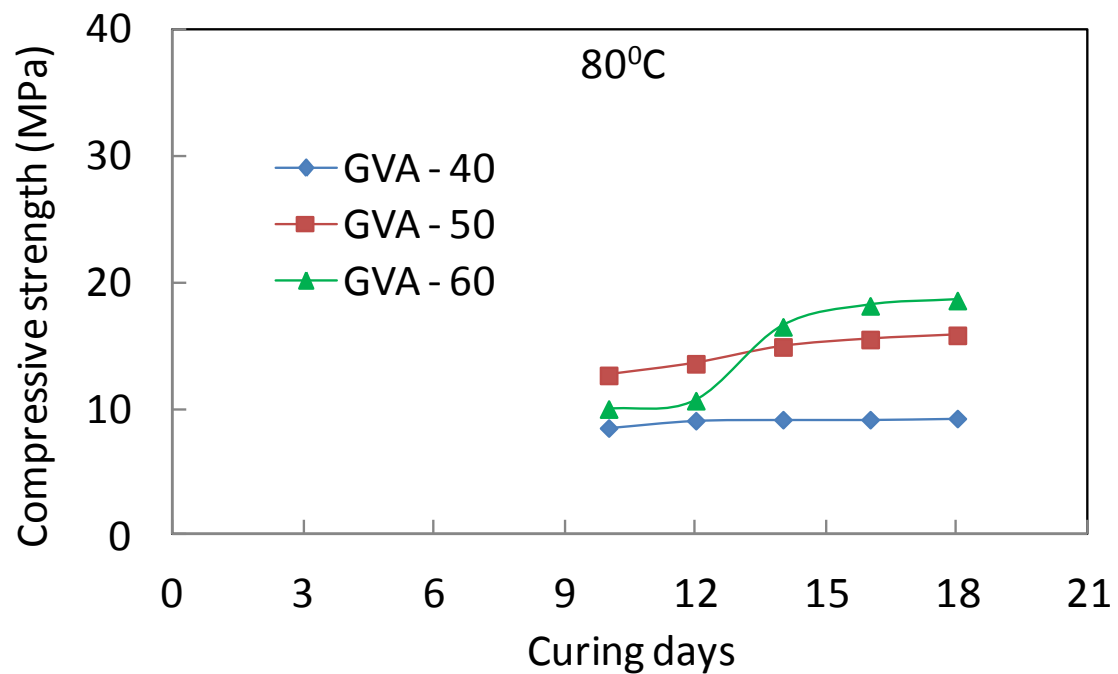


Fig. 5.22 Compressive strength variation with age

These factors are responsible for lower and delayed strength development. Volcanic ash used in making geopolymer mortar is less amorphous in nature. The degree of amorphousness of pozzolan is the most important parameter in polymerization reaction. Silica and alumina in volcanic ash do not readily dissolve during the first stages of polymerization reaction. This affects the succeeding stages of polymerization.

### **Shirasu balloon geopolymer (GSHB)**

The compressive strengths of Shirasu Balloon geopolymer subjected to curing temperature of 90°C (specimens prepared with mix proportion given in Table 5.9) are given in the Fig. 5.23. The compressive strengths are compared with different W/B of 40%, 50% and 60%. The Shirasu balloon geopolymer mortar shows a less compressive strength as compared to other geopolymer mortars. One of the reasons is less sufficient alkali activators and the other reason is thought to be Si/OH ratio. As the W/B increases the strength decreases, same as in the case of GSH. The initial hardening process is faster unlike GSH.

Shirasu balloon is processed form of Shirasu under fluidized bed. The surface nature of particles of Shirasu balloon is similar to fly ash and the degree of amorphousness is thought to be higher than Shirasu. Hence, the reactivity of Shirasu balloon is similar to fly ash. Shirasu balloon is very expensive considering the manufacturing process. It is used in the manufacture of expensive products used in construction industries and also used for medical purposes. These constraints pose infeasibility as binder in mortar or aluminosilicate source in geopolymer.

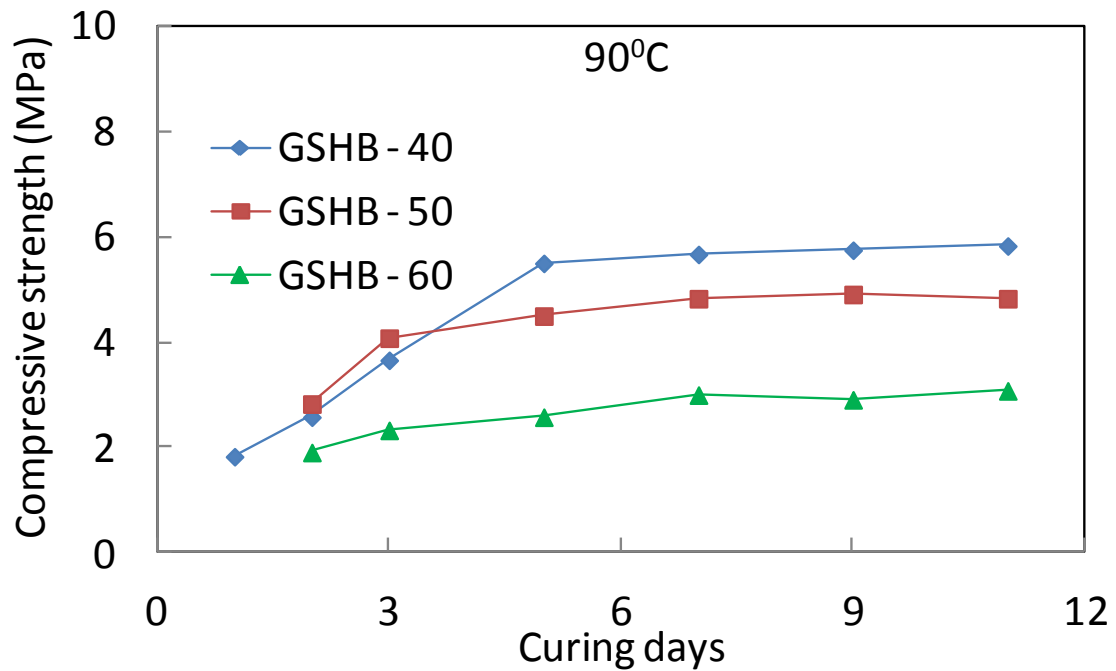


Fig. 5.23 Compressive strength variation with age

## 5.8 Summary

In this study, different types of pozzolans are used in making geopolymer mortar to understand the behavior of these pozzolans in polymerization reaction. The basic aim is to study the behavior of Shirasu concrete by comparing the properties with that of fly ash. As fly ash based geopolymer have been studied in the past, it is considered as base and control specimen to compare the performance of Shirasu. The parameters like W/B, amount of alkaline activators are kept constant for all geopolymer mix proportions for better comparison of results.

There are some similar trends in the results of geopolymer mortars with all kinds of pozzolans used. As the temperature of heat curing increases, the strength increases and

also increases the initiation of hardening. On the other hand, variation in W/B showed different results. The difference in compressive strength results is justified by the internal porosity of mortars. Shirasu based geopolymer has lower compressive strength than fly ash based geopolymer. Therefore, reactivity and strength development by fly ash is higher than Shirasu. Moreover, Shirasu geopolymer hardens at a very slow rate. This may be due to the lower degree of amorphousness of Shirasu.

Even though Shirasu and fly ash are pozzolans and have similar characteristics, they vary in some of the important parameters which effect strength development. The reason for the variation in results can be attributable to proportioning of materials. For this reason, silica to hydroxide balance in the mix is considered. Accordingly, strength tests on mortars with variation in Si/OH for GSH and GFA are conducted. The results obtained from the variation in Si/OH indicated that it is one of the important parameters to be considered. Also, along with suitable Si/OH, aggregate to aluminosilicate ratio is also confirmed to have an effect on strength development.

From the experimental study the strength of Shirasu geopolymer was low compared to fly ash geopolymer for same amount of alkaline activator. But when Si/OH was considered, the difference in strength between Shirasu and fly ash geopolymer reduced and the reactivity of Shirasu increased. Also as the sand to Shirasu ratio in the mix with constant Si/OH=9 decreased, the reactivity of Shirasu increased because of increase in paste volume. Therefore, different parameters have to be considered for increasing the reactivity of Shirasu. As Shirasu may have lower degree of amorphous and contain impurities, treating the Shirasu with acid or other reagents before using can be

considered. Also, difference in alkali is said to have effect on strength development. Regardless of type of pozzolan selected, however, higher concentrations of alkaline activators yield greater mechanical strength values. The pH level of the activating solution strongly influences the final cement performance. From an experimental study, it was confirmed that the strength measured from samples of pH 14 were five times greater than samples formed from pastes of pH 12; and it was concluded that a pH range of 13–14 was most suitable for the formation of geopolymers with higher mechanical strengths.

In the present study NaOH, which is popularly used as alkali in geopolymer, is used. KOH has been found to produce high compressive strengths and improved porosity in geopolymer cements. Since  $K^+$  is more basic than other activating ions, it possesses a greater potential for polymeric ionization in solution resulting in high reactivity of the prime pozzolan, a denser final product and a matrix formation capable of achieving increased compressive strength values. KOH can also produce higher pH with lower molarity. So, KOH can also be considered for further study on Shirasu geopolymer. Shirasu can also be milled or ground to higher fineness to improve the reactivity of silica and alumina. Therefore ground Shirasu can also be considered to improve reactivity of Shirasu in geopolymer.

## **Chapter 6**

### **CONCLUSION**

#### **(1) Pozzolanic Reactivity of Shirasu**

In the light of the experimental investigation and the results obtained for Shirasu and fly ash as binders in mortar, the mortar in which 10% of cement content is replaced by Shirasu results in high strength up to 1 year. The strengths of mortars with 20% and 30% replacement levels have slower rate of strength gain, but may gradually increase at a longer duration of curing. Shirasu replacement of 10% to 20% in binder seems to be appropriate for minimizing the reduction of strength. It is also evident that the altered mix proportion of Shirasu mortar considering water absorption not only gives good flow characteristics and workability for mortar but also long term strength gain by almost matching the strengths with that of ordinary mix proportion of Shirasu mortar without considering water absorption. As fly ash has ball bearing effect and causes less friction against particles, it increases the workability remarkably. It has also got higher reactivity than Shirasu at earlier ages of 90 days. But in the experimental results up to 1 year curing, Shirasu also matches the reactivity of fly ash and OPC at 1 year curing days indicating fairly good pozzolanic reactivity.

Long term pozzolanic reaction is confirmed from the experimental results and the strength of Shirasu mortars is expected to increase further beyond one year of curing. Hence long term strength property of Shirasu as binder increases the service life and

safety of structure where the structures are fully used at least after one year after construction. Partial replacement of Shirasu reduces the amount of cement used in total binder, thereby reducing the total heat liberated and overall cost of concrete. Introduction of Shirasu as binder also results in reduction of greenhouse emissions and contributes to sustainable concrete.

Shirasu as binder with different Blaine specific surface area and replacement ratio in mortar showed good pozzolanic reactivity at longer durations of curing. Finer Shirasu particles (higher value of Blaine) have higher reactivity even when the replacement ratio is as high as 30%. Therefore, fineness of Shirasu particles is an important factor to be considered when using Shirasu as cement replacement material. From the experimental results, it is expected that Shirasu can be used as binder with higher replacement ratios without affecting the properties of concrete by increasing the specific surface area of particles.

## **(2) Permeable Pavement Using Shirasu as Fine Aggregate and Recycled Gypsum as Binder**

Utilization of unused natural resource like Shirasu and recycled gypsum made from plasterboards in mortar for pavement has been attempted in the research work. The usage of Shirasu as aggregate helped in attaining good permeability required for pavement by its porous nature. As the water absorption is very high in case of Shirasu, care has to be taken in mix proportion and water required. It is also well known from previous researches that Shirasu shows pozzolanic reactivity in cementitious materials after a longer duration of curing. Therefore, in the comparison of results between Yokogawa and Koriyama Shirasu, Koriyama Shirasu has better results because it has lesser finer particles making the pavement permeable. Koriyama Shirasu has lesser fine particle fraction. As the fine particle fraction increases, the pozzolanic reactivity of Shirasu increases which consequently renders the mortar impermeable. Therefore, Koriyama Shirasu having lesser fine particles is expected to keep the permeability for longer duration.

From the experimental investigation, it is possible to propose mix proportion and construction methods for permeable pavement using Shirasu and recycled gypsum. Shirasu as fine aggregate in pavement can be an alternate to traditional pavement where sand is used and is expected to be as effective as traditional pavements. Shirasu develops long term strength sufficient for pavement and makes it permeable by its pore structure. From this experimental investigation, we can propose mix proportion and construction methods for permeable pavement using Shirasu and recycled gypsum.



Past researches confirmed that Hexavalent chromium is leached from cement used in permeable pavement. Therefore in this research permeable pavement using gypsum and /or magnesium oxide as binders with cement and Shirasu as fine aggregate is attempted and hexavalent chromium leached from the specimens are analyzed. The experimental results confirm that hexavalent chromium is leached by cement. Shirasu as fine aggregate is observed to leach higher amounts of hexavalent chromium due to its porous nature. Permeable pavement with sand may have better packing effect without compromising the standards and requirements for good pavement. Partial replacement of cement by pozzolans or chemical admixtures like gypsum or magnesium oxide can solve the problem of leaching by hexavalent chromium inhibition. Replacement of gypsum or MgO as binders can solve the problems encountered by using Shirasu. Therefore, permeable pavements can be effectively made by Shirasu as fine aggregate considering cement replacement materials like magnesium oxide and gypsum.

### **(3) Shirasu in Geopolymer**

Shirasu in geopolymer gave considerably good results when compared to fly ash. The variations of strengths with water binder ratio show contrasting results between different geopolymers. Also, the initial hardening of Shirasu geopolymer is delayed up to 6 days of heat curing. These results are attributed to the effect of different parameters like property of silica and its content in Shirasu, degree of amorphousness of Shirasu and also silica to hydroxide ratio in the mix. Shirasu is a pyroclastic flow deposit and fly ash is an industrial by-product. Hence, the chemical characteristics of silica and alumina in these pozzolans may vary largely. Silica and alumina in Shirasu particles may not be easily available for dissolution process with alkaline medium to form polymer at high temperatures. Dissolution process in the case of Shirasu may be lower because of possible impurities and oxide content over the years of deposition which delays the succeeding gelation and polymerization process.

Silica to hydroxide balance in the geopolymer mortar is observed to affect the compressive strength of the mortar irrespective of pozzolan type. Peak compressive strength is obtained in both Shirasu and fly ash based geopolymer mortars with mix proportions based on Si/OH suggesting that Si/OH is one of the important parameters to be considered in geopolymer mix proportion. Therefore, for a specific aluminosilicate source, optimum Si/OH can be selected including other parameters like paste volume, ratio of aggregate to aluminosilicate source and so on. Since concrete with no cement is possible in geopolymer technology, wide range of applications with significant reduction in cost, energy and greenhouse emission can be achieved using Shirasu in

geopolymer while contributing to sustainable concrete and environment.

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