Concrete with high-purity volcanic glass fine powder manufactured from pyroclastic deposit

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Abstract

Volcanic deposits, which are pozzolanically reactive, have long been known to improve the durability of concrete. Nevertheless, it has also been pointed out that the use of a natural pozzolan as a supplementary cementitious material (SCM) can pose problems of low workability and slow strength development. Also, in addition, its composition and physical properties have large variety and variability. We have been conducting studies on the total utilization of volcanic deposits for applications suitable for respective properties by classifying them by floating speed difference and particle diameter. It is reported that sorting out particles less than 2.4 g/cm^3 by dry gravity classification and removal of smaller clay fraction by dust collector is technically effective to recover high purity volcanic glass from pyroclastic flow deposits called “Ito-Shirasu”, which is a local name for pyroclastic flow deposits in Japan. In this study, concrete containing high-purity volcanic glass powders with different finenesses are investigated regarding fresh properties, strength development, chloride ion penetration and CO_2 reduction. As a result, it was found that volcanic glass powders made an excellent contribution to the improvement of flowability comparable to fly ash, the enhancement of strength comparable to silica fume, and the restraint of chloride ion penetration. Volcanic glass powders can also contribute to the reduction of CO_2 emission because the content of Portland cement can be significantly reduced to obtain the same strength compared to concrete with 100% Portland cement. This study provides a possibility to produce high performance SCMs in volcanic regions worldwide from volcanic ejecta by sorting out a high purity volcanic glass by the same method.

Keywords Volcanic glass · Natural pozzolan · Supplementary cementitious material · Dry gravity classification

1 Introduction

A quest for supplementary cementitious materials (SCMs) with a reactivity allowing them to be used as a replacement for Portland cement has been underway worldwide, with industrial byproducts including ground-granulated blast-furnace slag and fly ash being globally applied to actual construction. However, an expected reduction in the output of such materials, particularly fly ash, which is a byproduct of coal-fired power generation, was pointed

out already in 2007 [1], amid the trend to cope with the environmental problems.

Though the term “pozzolan” is widely used today to describe a reactive material for concrete regardless of whether it is natural or artificial, it is derived from “pozzolana”, natural volcanic ejecta, which was used as a material for concrete in the Roman era. Volcanic ejecta and deposits, which are pozzolanically reactive, have long been known to improve the durability of concrete. No standard has been available for these materials due to them not being industrial products, with their physical

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properties widely varying. Volcanic ejecta and deposits have therefore not been actively employed for construction under the circumstances where laws and regulations require engineers to refer to standards. However, with a shift from specification codes to performance-based codes in sight, active use of natural resources in the future of North America has been highlighted [2].

Nevertheless, it has also been pointed out that the use of a natural pozzolan as a supplementary cementitious material can pose problems of low workability and slow strength development [3]. Also, in addition to the low performance as a natural SCM, its composition and physical properties are widely variable [4] and significantly scattered [5] when compared with industrial byproducts.

The wide variety of natural pozzolans are classified by their origins as shown in Fig. 1. They are broadly divided into two categories: primary volcanic and sedimentary. Diatomaceous earth, hydrothermal siliceous sinters, and detrital sediments belonging to the sedimentary category. The volcanic category includes zeolitized tuff, or volcanic tuff, which are also altered by diagenetic processes. Excepting the group of diatomaceous earth, all natural pozzolans are derived from volcanic rock and volcanic minerals [6]. In many cases these are studied and used as they are, through the processes of pulverization and classification (mostly into particles smaller than 45 μm) [6]. However, most of these natural pozzolans contain such

inert minerals as quartz and feldspar, along with amorphous silicate (volcanic glass, VG), which causes reactivity.

Pyroclastic flow deposits referred to as “shirasu” cover a wide area, forming extensive pyroclastic plateaus with a layer about 10–200 m thick in the southern regions of Kyushu, Japan. The greatest amount of shirasu sediment, which is estimated to have a volume of 75 billion m^3 , is the Ito pyroclastic flow (A-Ito) that erupted out 29,000 years ago. This “Ito-shirasu” covers an area of about 3427 km^2 , and it contains non-welded pyroclastic flow sediment, which includes crystalline minerals, VG, and clay fractions. It is said that utilizing Ito-shirasu as an industrial resource is very difficult for these impurities [7]. According to an origin-based classification, Ito-shirasu is included in the group of unaltered pyroclastic materials. There have been few practical trials to use Ito-shirasu as fine aggregate, but a house built with Ito-shirasu concrete won the 2017 American Concrete Institute overall “Excellence” award [8]. Despite their environmental advantage, significant barriers remain to widespread adoption of Ito-shirasu in place of natural sand and crushed sand. A major barrier is related to the typical properties of natural pozzolans; low fluidity due to high fineness and angular particles. It was also reported that Ito-shirasu concrete causes higher shrinkage than controls [9]. In addition, its low density (2.0–2.2 g/cm^3) and high water absorption (2.5–9.2%) for fine aggregate are other barriers by laws and standards (JIS).

Fig. 1 General classification scheme of natural supplementary materials. Processing usually involves crushing grinding, and size separation, mostly under 45 μm . Modified after [4]

We have been conducting studies [10–14] on full utilization of Ito-shirasu by classifying it into various physical properties for various applications as construction materials. Equipment referred to as an air table is used for this classification. Figure 2 shows its mechanism. Its winnowing with the action of the vibration fluid bed can classify particles by their floating speed difference and particle diameter with low energy consumption.

We have previously blended the heavy particle and heavy dust fractions dry-classified by the air table from Ito-Shirasu, and found that the blend exhibited normal workability as fine aggregate equivalent to that of crushed sand [10]. Through this method using an air table, the amorphous content of the sorted light dust increased to 88% when that of raw material is about 60%. Furthermore, based on the analysis of the mineral composition and amorphous content of sorted light dust by Rietveld analysis, sorting out particles lighter than 2.4 g/cm^3 by the air table and removal of the smaller clay fraction by a bag filter is technically effective to recover high-purity

Fig. 2 Mechanism of air table; dry gravity classification. The particles are almost classified according to the density and diameter

Fig. 3 Distribution of shirasu and location of sampling site

VG from the raw material [11]. The authors demonstrated that, by pulverizing this high-purity VG to powders (VGP) with a mean particle size of around $1 \mu\text{m}$, a slump flow and 7-day and later strength equal to or greater than silica fume can be obtained when used for concrete at a water to binder ratio (W/B) = 0.2, even with smaller dosages of chemical admixtures. When used at W/B = 0.6, the concrete demonstrated excellent strength development from an age of 7 days even when up to 20% of normal Portland cement was replaced with VGP. That concrete also showed no reduction in the carbonation rate coefficient, indicating extremely high resistance to chloride ion penetration [10]. However, how the characteristics of VGP such as particle size, influence its behavior in a concrete mixture was overlooked, and whether or not dry classification by this method is effective only for Ito-shirasu was unclear in the previous study.

First, this study aims to verify whether the effect of dry classification of volcanic deposits by an air table is limited only to Ito-Shirasu, which spreads over Southern Kyushu of Japan, or whether it is more universal, by analyzing powder properties. Second, concrete containing VGP with different fineness is investigated from a more practical aspect.

2 Test materials and experimental program

2.1 Raw material and manufacturing process of VGP

Ito-shirasu used in this investigation was delivered from Kanoya-city, Kagoshima Prefecture in Japan by a mine operator without any pretreatment as shown in Fig. 3. The mineral compositions of the particle size fractions and the chemical composition of the raw material reported

Fig. 4 Mineral composition of particle size fractions and chemical composition of Ito-shirasu

in the previous research [10–14] are presented in Fig. 4. According to previous studies from resource engineering [15], Ito-shirasu is perfectly divided into crystalline minerals and amorphous phase through heavy liquid separation using zinc bromide ($\rho = 2.4 \text{ g/cm}^3$). Therefore, as to mineral components in this figure, the fractions over and under 2.4 g/cm^3 are defined as crystalline and amorphous, respectively. The fraction under 1.5 g/cm^3 in particular is defined as pumice based on the definition of lightweight aggregate by JIS A 5002.

Similarly to a former report [12], the test material was prepared by drying the part passing a 5 mm sieve to a water content of 1% or less. Figure 5 shows details of the classifier used. This equipment consisting of an air table along with a cyclone and dust collector classifies the material into five components. The classifying conditions include the material feed, pore size of the sieve, concavo-convex shape, inclination angle, rotation frequency, vibration amplitude, and air flow. The density and size of each component can be adjusted by setting these conditions [9]. The particles are classified according to the density and mean size as listed in Table 1 along with the recovery rate. Most crystal minerals are recovered as heavy particles

Table 1 Recovery rate, density and mean size of components

	Coarse crystalline	Fine crystalline	Pumice	VG	CF
Recovery rate (%)	12	21	19	46	2
Density (g/cm ³)	2.63	2.66	1.81	2.36	2.37
Particle mean size (μm)	1137	330	742	83.5	4.1

Fig. 6 Particle size distribution of VG and CF

1 mm or more in diameter and heavy dust less than 1 mm in diameter, while pumice is recovered as light particles. Among the light dust, fine particles recovered by the cyclone include high purity VG. The super fine part not recovered at the cyclone is recovered by the dust collector as the clay fraction (CF).

Figure 6 shows the size distributions of high-purity VG recovered by the cyclone and CF recovered by the dust collector measured by a laser diffractometer. The mean size of the fraction recovered by the dust collector is $4 \mu\text{m}$, representing the fine particle fraction slightly contained in the ore, though the two curves partly overlap due to dry classification.

The sorted high-purity VG and CF were crushed and classified as shown in Fig. 7. High-purity VG primary-crushed by a roller mill into a powder (VGR) is pulverized and classified using three devices: a jet mill to recover RJF

Fig. 5 the dry classifier used. An air table along with cyclone and dust collector classifies Ito-shirasu into five elements

Table 2 Materials used

Material	Properties	Marks
Binder		
Cement	Normal portland cement, density: 3.24 g/cm ³	N, NPC
	Low-heat portland cement, density: 3.24 g/cm ³	L, LPC
SCM	VGP, SF, FA	SCM
Fine aggregate	Crushed lime, density: 2.67 g/cm ³	S1
	Crushed tight sand, density: 2.62 g/cm ³	S2
Coarse aggregate	Crushed tight sand, density: 2.64 g/cm ³	G1
	Crushed lime, density: 2.70 g/cm ³	G2
Chemical admixture	High-range water-reducing admixture	SP1
	Air-entraining and high-range water-reducing admixture	SP2
	Air-entraining and water reducing admixture	SP3
	Air-entraining admixture	AE

Table 3 Factors and level, mixing proportions

Series	W/B	Cement	W (kg/m ³)	SCM/B (%)	S1:S2	S/a (%)	SCM used	Chemical admixture used	Target air content (%)	Target slump (cm)
I	0.20	L	160	10	4:6	45.2	SF + 6 VGP	SP1	2.0 ± 1.0	Slump flow 65 ± 10
II	0.50	N	167	25	2.5:7.5	42.8	FA + 6 VGP	SP2 + AE	5.0 ± 1.0	Slump 18 ± 2.5
III	0.60	N	183	5 10 20	2.5:7.5	50.8	RF RC VGR	SP3 + AE	5.0 ± 1.5	Slump 18 ± 2.5

In Series IV, the relational expressions between the binder-water ratio (B/W) and the 28-day compressive strength were experimentally determined to evaluate the environmental performance of concrete containing VGP on a practical basis. Tests were conducted at a ready-mixed concrete plant with actual shipping experience. All materials excepting VGP were the same as those normally shipped from the plant. Trial mixtures of RF, RC, and VGR were prepared with a fixed replacement ratio and three levels of W/Bs. Table 4 tabulates the test levels, proportioning factors, and fresh test results. The replacement ratio was 20% for RF, RC and VGR. RF was also tested with replacement ratios of 5% and 10%. The target slump and air content were 18 ± 3 cm and 4.5 ± 1.5%, respectively, for all mixtures. Compression tests were conducted at 28 days after standard curing.

3 Results

3.1 Chemical composition and ignition loss

Table 5 tabulates the results of chemical composition and ignition loss measurements. As shown in Fig. 8, the

SiO₂ content of both VGP and clay powder negatively correlate with both the ignition loss and Al₂O₃. The SiO₂ content and ignition loss of VGP are greater than 72% and lower than 3%, respectively, but after pulverization and classification, the SiO₂ content tends to slightly decrease in the fine powder fraction and slightly increase in the coarse powder fraction, with the difference being around 2%. As for clay powder, the SiO₂ content and ignition loss of CF are 65% and 4.5%, respectively, but the difference between those of the fine powder fraction (CFJF) and coarse powder fraction (CFJC) after pulverization and recovery are greater than those of VGP, being around 10% for SiO₂ content and around 3% for ignition loss. The Al₂O₃ content shows a similar trend.

VG is subjected to weathering action of water, undergoing hydration and elution, and follows a weathering sequence shown in Fig. 9, ultimately being modified to a clay mineral (halloysite, kaolinite and so on) [16]. SiO₂ is prone to elution through chemical changes, leaving compositions rich in Al₂O₃. Clay powder can therefore be regarded as being in a later stage of weathering in terms of chemical composition than VGP. In either case, fine powder shows a composition at a later stage of

Fig. 9 Weathering sequence of VG **Fig. 10** Thermogravimetric curves of VGP and clay powder

weathering than coarse powder, with the difference between fine and coarse powders of clay powder being greater.

3.2 Properties of adsorbed water

Figure 10 shows the thermogravimetric curves of three types of clay powder and three types of VGP from among the results of thermogravimetric analysis tests. The mass losses of CFJF and CF are significant, being 8% and 6%, respectively. Those of CFJC and RJF are similar at around 4%, but their ignition losses differed at 3.4% and 2.8%, respectively. This is presumably because the mass loss of RJF during drying at 105 °C for pretreatment before ignition loss measurement is greater as shown in the different low temperature ranges of their TG curves. The mass losses of RJC and VGR are both below 3%, demonstrating similar trends to the ignition loss results. Since VG derived from magma is reported to contain absorbed water, undegassed water, structural water equivalent to ignition loss whereas in a lot of cases ignition loss includes CO_2 as well [17], the losses in the TG curves are considered to be attributable to reduction in the moisture content, but the differential thermogravimetric curves shown in Fig. 11 demonstrate different trends of the peak temperatures of dehydration. One peak is found at around 250 °C for VGP including those not shown in the figure. This is a typical peak of VG [18]. The shift of this temperature toward a

Fig. 11 Differential thermogravimetric curves of VGP and clay powder

lower temperature as the sample is crushed to smaller particles [18] was also confirmed in the tests. For clay powder, peaks are found at less than 100 °C, around 250 °C, and 450 °C. The large peak at less than 100 °C is a tendency observed in allophane, an amorphous clay of weathered VG, indicating the presence of physical adsorbed water or interlayer water, which result from weathering-induced hydration and are not dehydrated by vacuum drying. Similar water is also found to be present in CF and CFJF.

At the peaks of 450 °C, slight endothermic shoulders are observed in all clay powders and in DTA as well. These are considered to be the dehydration of water bound by further hydration or of structural water (hydroxyl), suggesting an indication of clay mineralization [16].

Figure 12 shows part of the obtained water vapor adsorption isotherms. The adsorption and desorption

Fig. 12 Thermogravimetric curves of VGP and clay powder

curves of RJF are separated, being hysteretic similar to Type II or Type H4 that suggest the presence of slit-shaped pores and micropores according to the classification by IUPAC [19]. CF shows hysteretic curves close to Type III or Type V, with adsorption being small in low pressure ranges less than 0.1, which demonstrates that adsorption does not occur while the interaction between vapors is greater. The total adsorption of CF is high, though its hydrophily can be low, with the difference between adsorption and desorption being large. Therefore, once water is adsorbed, it tends to be hard to be desorbed. Regarding TG curves for which the pretreatment is vacuum drying, CF shows a dehydration peak of ΔTG at less than 100 °C. Therefore, the adsorbed water is mostly not desorbed at normal temperatures and low pressure, demonstrating properties close to allophane, which is used as a desiccant-adsorbent. Table 6 shows the BET specific surface determined from the water vapor adsorption at a pretreatment temperature of 105 °C and the nitrogen gas adsorption at a pretreatment temperature of 300 °C. CF was incalculable, as no linearity in the plots was found in the relative pressure range of 0.05–0.35. In contrast to SF, VGP and FA show BET specific surfaces by water vapor adsorption greater than that by nitrogen adsorption. In vapor adsorption, water is adsorbed selectively by hydrophilic sites, whereas nitrogen is an adsorbate that covers the entire powder surfaces

uniformly. The surface physical properties can therefore be discussed by using different adsorbates. Since the BET specific surface is calculated in the relative pressure range of 0.05–0.35, the amount of water vapor adsorption of VGP in the low pressure range turned out to be great due to its high hydrophily.

3.3 BET specific surface area and adsorption

Figure 13 shows the relationship between the mean particle size and the BET specific surface. The BET specific surface of VGP increases as the mean size decreases. On the other hand, clay powder shows no particular trend between the mean particle size and the BET specific surface. The BET specific surfaces of CF and CFJF are particularly large, being twice as large as that of VGP with similar mean size. The state of particle surfaces can differ from that of VGP.

Figure 14 shows the relationship between the BET specific surface and the MB adsorption. The BET specific surface and MB adsorption of VGP are closely correlated, with all sizes meeting the requirement to be not more than 1.20 g/100 g (12.0 mg/g) by EN 197-1: 2000 for the MB adsorption of limestone as a cement component. On the other hand, clay powders exceed this limit, with the

Fig. 13 Relationship between mean particle size and BET surface area of VGP and Clay powder

Table 6 BET surface area determined from water and nitrogen

Sample	VGR	RJF	RJC	RXF	RXC	RF	RC	CF	SF	FA
Water adsorption BET (m ² /g)	10.0	41.9	11.2	23.6	8.4	18.6	6.4	–	14.4	7.1
Nitrogen adsorption BET (m ² /g)	7.1	16.1	4.2	12.4	5.1	10.7	3.7	31.4	20.2	1.5

Fig. 14 Relationship between BET surface area and MB adsorption of VGP and Clay powder

adsorption tending to be above the approximate line for VGP.

Fig. 15 Relationship between BET surface area and MB adsorption of VGP and Clay powder. Here, σ is average of MB value, ρ is standard deviations

Focusing on the fact that silica is lost during the process of weathering, leaving alumina, the ratio of SiO_2 to Al_2O_3 (silica-alumina ratio) has been proposed as a most simple index to the degree of weathering, when the parent rock is the same [20]. Figure 15 shows the relationship between the silica-alumina ratio and the MB adsorption per unit BET specific surface. The chemical compositions of CFJF and CF represent particularly high degrees of weathering among the clay powders. Their MB adsorption is also 30% greater than that of VGP. When compared with CFJF and CF, the degree of weathering of CFJC is closer to that of VGP, but the value of adsorption is nearly twice as large as that of VGP. As for VGP, the degree of weathering of fine powder is slightly higher than coarse powder in terms of chemical composition, but their MB adsorptions can be regarded as being on the same level from their respective mean values and standard deviations. The adsorption of a polycarboxylate-based dispersant per unit area of powders of the same types (i.e., powders with the same compositions) is reported to be constant [21]. If this applies to MB, then fine and coarse powders of VGP can be regarded as the same powder from the aspect of dispersant adsorption, but clay powder cannot be regarded as the same type as VGPs. Also, the unit adsorption of CFJC is the largest, though its degree of weathering is not as high as CF and CFJF.

3.4 Fresh properties of concrete

Table 7 gives the fresh properties immediately after mixing and chemical admixture dosage of Series I. All VGPs are found to provide slump flows equal to or greater than SF with smaller chemical admixture dosages. In comparison with SF with a mean diameter of $0.1 \mu\text{m}$, the size of VGP is large. It is therefore presumed that agglomerations are prone to be dispersed due to the small van der Waals forces, requiring a small chemical admixture dosage. The time to 50-cm flow of the coarse powders is longer than that of fine powders, with substantial viscosity and dilatancy to cause resistance to shoveling with

Table 7 Fresh properties and chemical admixture dosage of Series I

Type pf SCM/BET surface area (m^2/g)	Slump flow (cm)	Air (%)	Time to 500 mm flow (s)	Time to end-of-flow (s)	SP1 dosage (B * wt%)
RJF/16.1	74.0×74.8	2.1	5.3	97	1.40
RXF/15.2	73.2×75.0	2.1	5.8	118	1.40
RF/12.0	73.8×72.2	1.8	5.5	92	1.40
RJC/4.2	74.0×73.8	1.8	6.3	95	1.30
RXC/5.1	72.4×71.1	1.9	6.8	102	1.20
RC/3.6	69.8×68.2	1.9	8.3	103	1.20
SF/17.7	69.0×68.0	2.9	4.3	79	1.60

a cement shovel. Though the time to 50-cm flow with the three fine powders is longer than that with SF, the consistency was sufficiently practicable. Powders with a BET specific surface of $12 \text{ m}^2/\text{g}$ or greater contain sufficient amounts of fine particles to fill the spaces between cement particles, increasing the packing factor of the binder. This presumably achieves a microfiller effect comparable to SF. Based on these results, it is judged that, in fresh concrete with a W/B of around 0.2, fine powders with a BET specific surface of $12 \text{ m}^2/\text{g}$ or more provide a flowability-improving effect, while the effect is less evident with coarse powders with a BET specific surface of $5 \text{ m}^2/\text{g}$ or less.

However, it can be said that VGP is a supplementary cementitious material that is expected to produce a sufficient effect of improving the workability of low W/B mixtures as demonstrated in the present results, provided that its physical properties including grading are rectified during the process of crushing and classification and that impurities including clay minerals are removed.

Table 8 gives the fresh properties and chemical admixture dosage of Series II. The mixing time was the same for all VGPs. The dosage of the high-performance air-entraining and water-reducing admixture for fine powders to achieve the target slump is higher than FA, whereas the admixture dosage to achieve the target slump and air content with coarse powders was the same as SF. The use of VGP reduces the slump flow by 15%, leading to fresh concrete with a high yield value. This is presumably due to the effect of the angular shape of crushed VGP particles in contrast to spherical FA particles. However, coarse powders with a BET specific surface of $5 \text{ m}^2/\text{g}$ or less show sufficiently practicable viscosity comparable to FA. It can therefore be said, from these results, that the target slump and air content were achievable in fresh concrete with a W/B of around 0.5 by using the same dosage of a chemical admixture as FA, which is effective in improving the concrete flowability.

Table 8 Fresh properties and chemical admixture dosage of Series II

Type of SCM/BET surface area (m^2/g)	Slump (cm)	Air (%)	SP2 dosage (B * wt%)	AE dosage (B * wt%)
RJF/16.1	18.5	5.8	1.10	0.40
RXF/15.2	19.5	5.8	1.10	0.40
RF/12.0	19.0	5.6	1.10	0.40
RJC/4.2	19.5	5.8	0.83	0.40
RXC/5.1	19.0	5.7	0.83	0.40
RC/3.6	18.0	5.5	0.83	0.40
FA/1.4	20.0	5.9	0.83	0.40

Fig. 16 Compressive strength with a W/B of 0.2 in Series I

3.5 Strength development

Figure 16 shows the compressive strength with a W/B of 0.2. At an age of 4 weeks, the strength with VGPs is equal to or higher than with SF. At 13 weeks, the strength is equal to or lower than SF. It has been reported that, if the W/B is constant, then a 1% increase in the air content reduces the strength by 4–6%. The air content with SF is higher than that with VGP by around 1% in a fresh state. It follows that, even if the strength with VGP is reduced by 5%, it can be regarded as roughly comparable to SF up to 4 weeks. Figure 17 shows the compressive strength with W/B = 0.5. The strength with fine powders is approximately 20% higher than with FA, while that with coarse powders is equivalent to that with FA, at all ages.

Figure 18 shows the strength development. With W/B = 0.2, the strength gains with SF from 4 to 13 weeks are greater than with any of the VGPs, but the slopes from 7 to 28 days are similar for all specimens. With W/B = 0.5, similar tendencies are found in the strength development over time in both cases of FA and VGP.

Fig. 17 Compressive strength with a W/B of 0.5 in Series II

Fig. 18 Strength development

Fig. 19 VGP's BET specific surface and the relative strength ratio to SF at W/B=0.2

Figure 19 shows VGP's BET specific surface and the relative strength ratio to SF at W/B=0.2. The strongest correlation between the relative strength ratio and the BET specific surface is observed at 1 week, with the strength being equivalent with SF even at a BET specific surface of 3 m²/g. With a BET specific surface of 12 m²/g or greater, the strength is equal to or higher than that with SF. However, both the slope of the approximate lines and the correlation coefficients decrease over time, ending up with a strength equivalent to that with SF with all specific surfaces at 4 weeks and a strength equal to or lower than that with SF even with 15 m²/g or more at 13 weeks. The reaction rate of SF in place of 10% of cement in a paste with W/B=0.22 is reported to rapidly increase up to 7 days and slows down thereafter [22]. Though the strength development mechanism of VGP can slightly differ from that of SF due to the different amorphous content and chemical composition, it is presumed that the strength test results

of VGP correlate well with the BET specific surface at 1 week and delayed reaction of particles with smaller BET specific surfaces proceeds thereafter. However, the results that strength ratio to SF is 100% or higher up to 4 weeks but is less than SF at 13 weeks imply the effects of factors other than reactions, such as void percentage. Elucidation of strength development related to age remains a subject for future research.

Figure 20 shows the relative strength ratio to FA with W/B=0.5. A closer correlation than 0.2 W/B is observed between VGP's BET specific surface and strength ratio to FA, though with a slight scatter at 13 weeks. According to a former research on pastes with a replacement ratio of 20% and a W/B of 0.4, the reaction ratio of Type II fly ash specified in JIS A 6201 is around 10% at 7 days and 42–53% at 555 days, being affected by the amount, chemical composition, and fineness of the glass phase [23]. Since the only difference among the six types of VGPs in the present study is fineness, the obtained strength development presumably corresponds with the BET specific surface, which is closely related to fineness. However, the slightly low strength ratio to FA at 13 weeks requires further observation of long-term strength to elucidate the strength development mechanism.

3.6 Resistance to chloride ion penetration

Figure 21 shows the results of immersion tests on concrete specimens in 10% saltwater for 42 weeks after 4-week water curing. The concretes with W/B=0.6 were OPC and concretes containing RF, VGR, and RC in place of 20% of cement. The chloride contents in the surfaces and deeper inward of concrete containing VGPs are significantly lower than those of OPC. Concrete containing RF or VGR not only

Fig. 20 VGP's BET specific surface and the relative strength ratio to FA at W/B=0.5

Fig. 21 Chloride ion penetration in 10% saltwater for 42 weeks

shields the penetration of chlorides at a depth of 20 mm but also inhibits its penetration at 10 mm. Even concrete containing RC with the smallest BET specific surface is found to shield chloride ion penetration at 35 mm. Though the shielding effect of RC is weaker than those of RF and VGR, it significantly improves the chloride ion resistance of concrete when compared with OPC. The apparent diffusion coefficients of OPC, RF, VGR, and RC regarding all chloride ions are 4.00, 0.16, 0.20, and 0.60 cm^2/year , respectively. VGPs with a larger BET specific surface show a smaller apparent diffusion coefficient of chloride ions. In the case of a replacement ratio of 20%, even the apparent diffusion coefficient of RC with a BET specific surface of approximately 3 m^2/g is less than 20% of that of OPC. The diffusion coefficients of VGR and RF with BET specific surfaces of approximately 7 m^2/g and 11 m^2/g , respectively, are less than 20% and less than 10%, respectively, of that of OPC.

3.7 W/B-strength relation and contribution to CO_2 reduction

Figure 22 shows the approximate lines calculated from the compression test results and the B/W-strength relational expressions. The relational expression for OPC in the figure is the expression adopted for the actual ready-mixed concrete made of the same materials and shipped by the plant. Due to approximation of trial mixtures with three levels by $n = 1$, the scatter of the results of 20%-replaced RF is wider than that of OPC approximated by $n = 4$. RF with a BET specific surface of 11 m^2/g shows a higher strength than OPC with the same B/W even with a replacement ratio of 5%, and the effect remains up to a replacement ratio of 20%. The strength of VGR with a BET specific surface of 7 m^2/g is slightly higher than OPC. That of RC with a BET specific surface of 3 m^2/g is slightly lower than OPC. In Series II, the strength development is comparable to fly ash with a W/B of 50% and replacement ratio of 25%. It can therefore be regarded

Fig. 22 B/W-compressive strength relation

as equivalent to general fly ash of JIS Type II, which is available on the market in Japan. A higher strength at 91 days is therefore expected.

Figure 23 shows the unit cement reduction determined from calculation by the relational expression for proportioning to achieve compressive strengths of 30, 40, and 50 MPa. The unit water content of OPC proportioning for general slump control is assumed to be 180 kg/m^3 , whereas the unit water content in the flow control using VGP is assumed to be 170 kg/m^3 . By assuming the proportioning control strength as 50 MPa, the cement content can be reduced by more than 100 kg even with a replacement ratio of 10% at which the carbonation rate coefficient decreases. With a 20% replacement, the cement content can be reduced by 150 kg. Also, with RC, the B/W-strength relational expression of which is lower than cement, the cement demand to obtain the same strength becomes smaller, as the replacement ratio is 20%. Reductions of more than 50 kg are therefore achieved at all strength levels.

Fig. 23 Unit cement reduction to achieve compressive strengths of 30, 40 and 50 MPa

4 Discussion and conclusion

In the field of natural disaster science, the refractive index of VG is used as an index to the progress of weathering of a cliff, as it increases under the effect of hydration. Also, the particle structure of a glass shard is explained as a structure consisting of a non-hydrated core surrounded by a hydrated rim, since the refractive index of crushed glass shards is widened toward the lower side [24]. VG is a most weatherable material, and the smaller the particle, the faster the weathering proceeds, changing to a different soft material under chemical weathering action [25]. In view of these findings and the results of the present study, Fig. 24 shows the particle properties and process of crushing/classification.

Both VG and CF have a structure with a hydrated rim on the surfaces, and layers closer to the surface are softer and more prone to be pulverized during the crushing process, tending to be recovered by a dust collector. This agrees with the fact that fine and coarse powders have different chemical compositions and ignition losses. Based on the adsorption per unit area and the results of thermoanalysis of CFJC, it is considered hydration proceeds more to the cores of smaller-size CF particles than VG particles. In particular, CFJF has a concentrate of highly weathered surface layer. In other words, crushing after removing heavily weathered fine particles is effective in manufacturing unweathered high purity VGP, which is a high performance SCM, from volcanic deposits.

Whereas basaltic magma with low viscosity causes moderate volcanic activity, rhyolitic magma is generally said to cause violent and explosive eruption [4]. In other words, magma with a large SiO_2 content is said to cause

explosive eruption. The deposits of volcanic materials excepting gasses are classified into three types: pyroclastic fall deposit, pyroclastic flow deposit, and lava. Pyroclastic fall deposit results from a Plinian eruption shown in Fig. 25, whereas pyroclastic flow deposit results from a pyroclastic flow.

A Plinian eruption, an explosive one represented by the eruption of Mount Vesuvius in 79 AD, forms an eruptive column made of gases, magma and rocks crushed to pieces, and fragments of minerals directly above the crater for half an hour to several days. The temperatures of this column higher than the surrounding atmosphere cause convection. The top of the eruptive column is formed where the density of the column equals the surroundings and spreads horizontally. Low-density particles including volcanic ash and pumice are horizontally blown by the wind and begin to fall when their speed decreases to the point of equilibrium between air resistance and gravity; 'terminal speed'. Since smaller particles are carried farther away due to their lower terminal speed, they are subjected to fractionation while flying. The material deposited near the crater is referred to as fall pumice. The material 2 mm or less in size is referred to as volcanic ash. Both are uniform in size and contain little crystal minerals or lithic fragments. There can be a case where weathered materials subjected to hydration are included, but high purity VG can be sorted out by the cyclone and dust collector of the present device for air classification.

On the other hand, collapse of an eruptive column leads to a so-called pyroclastic flow. A large-scale flow is formed by gravitational collapse of an eruptive column, which is regarded as a phenomenon of a rapid outflow of unclassified pumice, volcanic ash, and rock fragments with volcanic gases as shown in Fig. 26. Coarse particles tend to

Fig. 24 Particle contained in volcanic ejecta and deposits and their crushing process

Fig. 25 Diagram of Plinian eruption

Fig. 26 Diagram of Pyroclastic eruption

be entrapped among fine particles due to the weak classifying action.

Though such ejecta, which is also referred to as tephra, is derived from magma, it also includes 'accessory' materials derived from the old volcanic body near the magma reservoir and conduit and 'accidental' materials, which are fragments of the basement rock. Their quantitative ratios vary depending on the scale and pattern of eruption and distance from the eruption source. After deposition, extraneous materials from the surrounding ground can be normally included during various stages of turning into soil. In view of the use as a SCM in the field of concrete, pyroclastic deposits resulting from explosive eruption of magma with a high SiO_2 content are advantageous from the aspect of the amount of resources, but they simultaneously entail abundant impurities other than pozzolanically reactive VG.

Ito-Shirasu presently under study is a large-scale pyroclastic flow sedimentation with an estimated reserve of 75 billion m^3 , but amorphous materials including pumice were reported to account for around 60% based on heavy

liquid separation, while crystal minerals were approximately 40%. Also, the fine fraction of CF with a recovery ratio of 2% showed indications of weathering. According to the results of research into VG and other minerals contained in volcanic ejecta from Cascade Range in North America [26], the densities of pumice, glass shards, and lithic fragments were 0.7–1.2 g/cm^3 , 2.35–2.45 g/cm^3 , and 2.7–3.2 g/cm^3 , respectively. That of crystalline materials and crystal fragments was 2.6–5.2 g/cm^3 . Therefore, our findings from volcanic deposits in Japan that VG can be perfectly sorted out both with a density limit of 2.4 g/cm^3 and with a diameter limit of around 5 μm can be applicable to volcanic ejecta from Cascade Range. Physical densities of particles should fall in constant ranges when considering the mechanisms acting on volcanic ejecta—eruption of liquid magma onto the ground and rapid cooling thereafter, crystallization within the underground magma, rocks present on the ground, weathering after deposition, and so on. In that sense, this study provides a possibility to produce high performance SCMs in volcanic regions worldwide from volcanic ejecta, which have been regarded as a low performance material, by sorting out a high purity VG by the same method using an air table.

The findings regarding concrete made using VGP obtained in this study include the following:

1. Fresh properties

With a W/B of around 0.2, VGP powder with a BET specific surface of 12 m^2/g or more has a flowability-improving effect, while such an effect is judged as being weak with a BET specific surface of 5 m^2/g or less. With a W/B of around 0.5 or more, a replacement ratio exceeding 10% of VGP with a BET specific surface of 12 m^2/g or more increases the chemical admixture demand for achieving the target slump increases. With a BET specific surface of 5 m^2/g or less, however, the target slump and air content can be achieved with a chemical admixture dosage equivalent to JIS Type II fly ash with a replacement ratio of 25%.

2. Strength properties

With a W/B of around 0.2, the BET specific surface of VGP correlates with the strength, demonstrating the strength-developing performance equivalent to SF with a BET specific surface of around 5 m^2/g , and that equal to or higher than SF with a BET specific surface of 12 m^2/g . At four weeks, the correlation between the BET specific surface and strength becomes weak, demonstrating a strength-developing performance equivalent to SF. At an age of 13 weeks, the correlation becomes even weaker, with the strength being equivalent or lower than SF. With a W/B of around 0.5 or more, a strength equivalent to JIS Type

II fly ash is obtained with a BET specific surface of around 3 m²/g. The strength becomes 20% higher than fly ash with a BET specific surface of 12 m²/g or more, with correlation between the BET specific surface and the strength being observed up to 91 days.

3. Durability and CO₂ reduction

The use of VGP with a BET specific surface of around 3 m²/g at a replacement ratio of 20% provides sufficient resistance to chloride ion penetration, being sufficiently effective in reducing the amount of Portland cement consumption.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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