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Effects of desulfurized gypsum on shrinkage behavior of alkali-activated slag (AAS) and hybrid alkali-activated cement (HAC)

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ABSTRACT

This study reports the use of desulfurized gypsum (DSG) to mitigate the shrinkage problem of two typical alkali-activated materials (AAMs), i.e. alkali-activated slag (AAS) and hybrid alkali-activated cement (HAC). The effects of DSG type and content on the hydration kinetics, mechanical properties, autogenous/drying shrinkage, and microstructure evolution of the AAMs were investigated. Results indicate that DSG can retard the hydration process and reduce the formation of gel products. Incorporating DSG into AAM mortar leads to a reduction in both autogenous and drying shrinkage, showing better efficiency than normal gypsum. An insights into the mechanism underlying shrinkage for the DSG-AAM systems was gained through MIP, ¹H NMR,XRD,TG-DTG, and SEM-EDS analyses. It was discovered that the higher Ca/Si of gel (amorphous C-A-S-H) phase and the higher crystalline/gel phases ratio in the DSG-AAM systems contributed to mitigating drying shrinkage. In addition, the shift of gel pore and capillary pore size and distribution contribute the reduced shrinkage.

1. Introduction

Alkali-activated materials (AAMs) are regarded as a promising low carbon alternatives to Portland cement due to its reuse of industrial waste, low carbon footprint of manufacturing, comparable mechanical properties, and better corrosion resistance [1–3]. It is especially worth noting that the application of AAMs in fields such as artificial alkali-activated aggregates [4,5] and high-strength engineered geopolymer composites [6–8] has become a global topic of increasing interest. Among high calcium AAMs, alkali-activated slag (AAS) and hybrid alkali-activated cement (HAC) have garnered significant attention due to their high early strength, exceptional binding characteristics, and ambient temperature curing requirement [1]. However, the widespread application of AAMs is hindered by their tendency for large shrinkage. The behavior of shrinkage plays a crucial role in the durability of cementitious materials. Large shrinkage leads to cracks, not only reducing mechanical properties but also facilitating the intrusion of

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water and corrosive liquids, ultimately compromising the structural integrity of the material [9]. Although HAC paste exhibits lower shrinkage than AAS due to a higher crystalline phase content and a more favorable Ca/Si gel ratio, its shrinkage remains greater than that of traditional OPC [10]. The pore size distribution, hydration product characteristics, and relative humidity are critical determinants of shrinkage properties [11,12]. In the case of AAMs, significant shrinkage is primarily attributed to pore size refinement induced by alkali activators that causing elevated capillary pressure. On the other hand, the hydration products of AAMs primarily consist of amorphous gels with a low Ca/Si ratio, such as C-A-S-H and N-A-S-(H). The tendency for C-A-S-H gels in AAMs to collapse and recombine during drying is considered a critical factor contributing to significant drying shrinkage [13,14]. Addressing the issue of excessive shrinkage is imperative in order to facilitate the utilization of AAMs in large precast concrete members requiring high early strength and durability.

The strategies for mitigating shrinkage in AAMs discussed in previous studies primarily encompass internal curing, high temperature curing, and the use of shrinkage-reducing or expansion agents. Internal curing agents can mitigate autogenous shrinkage by supplying additional moisture to compensate for the voids resulting from self-desiccation. Elevated temperature curing has been shown to effectively reduce drying shrinkage in AAMs by enhancing the volume of fine porosity and internal water within the C-A-S-H gel under thermal curing conditions [11,15]. Shrinkage reducing agents (SRAs) can reduce the surface tension of pore solution in cementitious materials, thereby diminishing capillary pressure - a primary driving force behind shrinkage [16–19]. Expansion agents are an effective approach to reduce drving shrinkage by increasing the amount of crystals in hydration products [13]. Previous research has demonstrated that the incorporation of gypsum can mitigate the drying shrinkage of AAMs. This is attributed to the formation of expansion sulfate-rich products, such as ettringite, which partially counteracts the shrinkage in AAMs. The extent of shrinkage reduction is contingent upon the gypsum content: a 2.5 % gypsum addition exhibits negligible effects on shrinkage reduction, whereas a 5 % gypsum inclusion can achieve a 10 % decrease in shrinkage compared to pure AAM [20–22]. Desulfurized gypsum (DSG), a by-product of flue gas desulphurization in thermal power plants and coal-fired plants, mainly consists of CaSO4·2H2O with 10 %-20 % water. The current annual output of DSG in China exceeds 130 million tons [23]. DSG cannot be directly utilized in thermal power plants and requires appropriate storage, which is not an environmentally sustainable method of disposal. Collaborative preparation of cementing materials using multiple solid wastes has emerged as a viable solution for industrial solid waste management. Research indicates that DSG and industrial solid waste such as fly ash can be effectively utilized to produce high-quality cementing materials [24,25]. However, there is a lack of comprehensive studies on the drying/autogenous shrinkage of AAM with DSG, and the underlying mechanisms have yet to be elucidated. It is well established that the maximum allowable content of gypsum in cement-based materials is 5 % to prevent detrimental expansion [26]. Given the significant shrinkage observed in AAMs, further investigation into whether increased DSG can effectively compensate for this shrinkage value is warranted. To expand the knowledge base and extend the application of AAM, it is imperative to conduct a comprehensive study on the shrinkage behavior of AAM-DSG system and delve deeper into its underlying mechanisms.

The present study investigates the impact of DSG dosage and type on the drying shrinkage and autogenous shrinkage of AAS and HAC. The pore size distribution, phase composition, chemical composition, and microstructure of reaction products were characterized through ¹H NMR, MIP, XRD, TG-DTG, and SEM-EDS analyses. Furthermore, the mechanism of DSG on the shrinkage of AAM was evaluated and effective measures for reducing shrinkage were suggested.

2. Experimental programs

2.1. Raw materials and preparation

S115 grade ground blast furnace slag (GBFS) with a specific surface area of $452 \text{ m}^2/\text{kg}$, in accordance with Chinese standard GB/T 18046–2017 [27], was used as the primary raw material for this study. Additionally, PII42.5 ordinary Portland cement (OPC), following Chinese standard GB 175–2023 [28], was also employed. In order to further minimize energy consumption, unprocessed DSG was predominantly utilized for this research, while low-temperature (130°C) calcined DSG (CDSG) was used for comparison purposes. The main chemical compositions of GBFS and OPC are detailed in Table 1, and the X-ray Diffraction (XRD) patterns of the raw materials can be found in Fig. 1. Furthermore, the micro-morphology of DSG and CDSG is depicted in Fig. 2.

The sodium silicate activator with a modulus of 1.5 was prepared by water glass, sodium hydroxide pellets, and deionized water. ISO standard sand was used as fine aggregate.

Table 2 presents the mix proportions of various samples. An exploratory experiment revealed that AAM containing more than 20 % DSG exhibited efflorescence phenomenon and a large amount of unreacted gypsum; therefore, the selected content of DSG is 5 %,10 %,15 %, and 20 % of cementitious materials. The control groups consist of AAS and HAC.

Mortars with various compositions according to Table 2 were prepared for mechanical properties and shrinkage tests. These specimens were cured to a specific age in a standard curing chamber (at 20 ± 2 °C and humidity higher than 95 %).

The paste samples were mechanically crushed at different curing ages and then terminated with isopropyl alcohol. The isopropyl

Table 1
The main chemical composition of GBFS and OPC.

Туре	SiO_2	Al_2O_3	Fe ₂ O ₃	CaO	MgO	SO_3	K ₂ O	TiO ₂	Na ₂ O	MnO	P_2O_5
GBFS	28.19	14.25	0.33	44.60	7.95	2.31	0.48	0.75	0.43	0.46	0.02
OPC	21.22	10.9	5.82	51.78	3.12	3.97	0.63	0.70	0.26	0.79	0.37



Fig. 1. XRD patterns of raw materials.



(a) DSG

(b) CDSG



Table 2
Composition of experimental specimens.

Sample No.	Mass fraction/%									
	Slag	OPC	DSG	CDSG	Alkali-activator ($Na_2O\%$)	w/c	ISO sand			
AAS	100	0	0	0	5	0.4	200			
AAS1	100	0	5	0	5	0.4	200			
AAS2	100	0	10	0	5	0.4	200			
AAS3	100	0	15	0	5	0.4	200			
AAS4	100	0	20	0	5	0.4	200			
AASD	100	0	0	5	5	0.4	200			
HAC	80	20	0	0	5	0.4	200			
HAC1	80	20	5	0	5	0.4	200			
HAC2	80	20	10	0	5	0.4	200			
HAC3	80	20	15	0	5	0.4	200			
HAC4	80	20	20	0	5	0.4	200			
HACD	80	20	0	5	5	0.4	200			

alcohol was replaced at 1 and 24 hours, and the samples were removed a week later for vacuum drying. Thin slices with a particle size of 3–5 mm and flat surfaces were selected for SEM-EDS analysis, bulk samples with a diameter of 2–6 mm were used for MIP testing, and samples with a diameter less than 3 mm were ground and sifted with a 0.075 mm screen for XRD and TG testing.

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2.2. Experimental method

2.2.1. setting time

The setting time was determined in accordance with a Chinese standard GB/T 1346–2011-Test method for water requirement of normal consistency, setting time and soundness of the Portland cement. Standard consistency pastes were prepared, followed by testing the setting time using a Vicat apparatus.

2.2.2. Compressive strength

Compressive strength was determined according to the method specified in International standard ISO 1920–3–2004. The specimens were cured to 3 d,7 d,14 d and 28 d in the standard curing chamber for strength testing.

2.2.3. Drying shrinkage and mass loss

The drying shrinkage test was conducted in accordance with the Chinese standard JC/T 603–2004, which specifies the standard test method for drying shrinkage of mortar. Three 25 mm × 25 mm × 280 mm mortar prisms were prepared as a group to determine drying shrinkage and mass loss. The length of the mortar prisms was measured using a length comparator. The initial length of the specimen after 24 hours of standard curing was recorded, following which these prisms were placed in a drying chamber maintained at a temperature of 20 ± 2 °C and relative humidity of 60 ± 5 %. The drying shrinkage (ϵ_{ds}) of the prisms at different ages (2, 3, 7,14,21,28,35,42,49,56 days) was calculated using Eq.1.

$$\varepsilon_{ds} = \frac{L_0 - L_t}{250} \tag{1}$$

where L_0 represents the initial length and L_t represents the length at different ages.

The mass loss of specimens due to drying shrinkage was monitored daily during the first week, and subsequently at 2, 3, 7,14,21,28,35,42,49,56 days. The water loss (M_{wl}) was calculated using Eq.2.

$$\boldsymbol{M}_{wl} = \frac{\boldsymbol{M}_0 - \boldsymbol{M}_t}{\boldsymbol{M}_0} \times 100\% \tag{2}$$

where M_0 (g) represents the initial mass and M_t (g) is the mass of specimens at different ages.

2.2.4. Autogenous shrinkage

Autogenous shrinkage was determined using a non-contact corrugated pipe in accordance with the method outlined in ASTM C1698–2009 (2014) [29], which is the standard test method for autogenous strain of cement paste and mortar. The freshly mixed mortar was poured into a corrugated mold with a length of 420 ± 5 mm and diameter of 29 ± 0.5 mm, after which the mold was sealed and placed in a non-contact bellows autogenous shrinkage tester within a drying curing room maintained at a temperature of 20 ± 2 °C. The final setting time marked the commencement of the test, with length variations automatically recorded every 20 minutes until reaching a certain age. Autogenous shrinkage was also automatically calculated and recorded with less than 1 % relative standard deviation.

2.2.5. Low-field ¹H NMR test

The MAG-MED PM-1030 analyzer operating at a frequency of 9.82 MHz was used for the testing process. Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences were employed to determine the transverse relaxation time (T_2) of AAMs. Each CPMG data set consisted of 3000 echoes with an echo time of 80µs, a total relaxation delay of 240 ms, and 64 scans per test. The T_2 transverse relaxation time was used to monitor the mobile water content, including capillary water and gel water, within the pastes during a measurement period ranging from hydrating for 10 minutes to 24 hours [30].

2.2.6. XRD analysis

The crystal types and quantities of reactants, such as ettringite, were determined through XRD analysis. Powder samples were positioned on the Cu target of the XRD-7000 X-ray diffractometer to generate the XRD pattern for each sample. The scan speed was set at 2.5 (°) /min, with 2θ ranging from 5 to 80° .

2.2.7. Thermogravimetric(TG) and derivative thermogravimetric (DTG) analyses

The specimens that have been cured to a certain age were subjected to thermogravimetric analysis in a N2-atmosphere using the NETZSCH STA 2500, with a heating range of $30-1000^{\circ}$ Cand a heating rate of 10° C/min.

2.2.8. Mercury intrusion porosimetry (MIP) analysis

The Aotupore IV 9500 automatic mercury porosimeter, capable of testing pore diameters ranging from 5 to 340 000 nm, was used for the characterization of total porosity and pore size distribution in various specimens. Mercury with a surface tension of 485 dynes/ cm and a contact angle of 130° was employed for these measurements.

2.2.9. Scanning electron microscopy with energy-dispersive spectrometry (SEM-EDS) analysis

The morphology and chemical composition of the reaction products from different samples were characterized using SEM (Zeiss Sigma 300) and EDS (Oxford Xplore 50).

3. Results and discussion

3.1. Setting time

The impact of DSG on the setting time of various alkali-activated systems is illustrated in Fig. 3. It can be observed that the incorporation of DSG effectively prolongs both the initial and final setting time of AAS and HAC pastes, whereas the two systems exhibit distinct delaying trends. In AAS system, both the initial and final setting times increase with an escalation in DSG dosage, particularly when the content surpasses 10 wt%. Among all samples, AAS4 demonstrates the maximum setting time, with an initial setting duration of 174 min and a final setting duration of 432 min. A comparison between AAS1 and AASD reveals that CDSG has a more pronounced effect on setting time in AAS system. Conversely, within the HAC system, although adding DSG delays its setting time like in AAS, both initial and final settings are shortened rather than prolonged as DSG content increases - contrary to what is observed in AAS. Notably, HAC mixed with 5 wt% DSG exhibits the longest overall setting time: an initial set at 167 min and a final set at 298 min. Previous research indicates that HAC exhibits a longer setting time compared to AAS at a DSG content of 5 %, corroborating the findings of the present study [20]. It is worth mentioning that DSG and CDSG display similar retarding effects on HAC system performance, however, CDSG has more obvious retarding effect than DSG in the AAS system. In summary, introducing DSG effectively delays both the setting and hardening processes within AAM.

3.2. Compressive strength

The compressive strength of various DSG-AAM mortar is presented in Fig. 4. With an increase in the addition of DSG, the compressive strength of DSG-AAM systems decreases, which is consistent with previous research results [19,31]. Comparing the strength development between AAS and HAC systems reveals that DSG significantly influences the 3 d and 7 d strength of both systems. For the 14 d and 28 d strength, AAS with 10 % DSG show a visible decrease, reaching its lowest point at 15 wt% DSG content before increasing again with further dosage increment. In contrast, the HAC system exhibits different strength development: the strength for all ages continues to decrease as DSG content increases. The strength development of both AAS and HAC systems is found to be superior when using DSG in comparison to CDSG. The introduction of DSG leads to a loss in the strength of AAMs, and this reduction is more pronounced in late strength of HAC system compared to AAS system. The underlying reason of the reduction in strength needs to be explained by the hydration process and hydration products.

3.3. Drying shrinkage and water loss

The influence of DSG on the drying shrinkage for AAMs over a period of 56 days is depicted in Fig. 5. It can be observed from Fig. 5 (a) that the addition of more than 10 % DSG can partially alleviate the drying shrinkage of AAS, although AAS3 and AAS4 exhibit higher shrinkage values than that of AAS during the first two weeks. However, increasing the DSG content does not further reduce the drying shrinkage value, instead, 15 % DSG achieves the lowest shrinkage level. Moreover, it is evident that AAS with CDSG demonstrates lower drying shrinkage compared to an equivalent amount of DSG. In Fig. 5(b), it is found that the magnitude of drying shrinkage in HAC mortar gradually decreases with increasing DSG dosage, with a maximum reduction reaching approximately 50 %. However, HAC with CDSG exhibits higher drying shrinkage than when using an equal dosage of DSG, which contrasts with observations made in AAS mortars. In addition, the drying shrinkage value of HAC is observed to be smaller than that of AAS, and this trend



Fig. 3. Setting time of different AAM pastes.



Fig. 4. Compressive strength of different AAM mortars.



Fig. 5. Drying shrinkage of different AAM mortars.

persists even when DSG is incorporated, which is consistent with previous research[20].

Mass loss is considered as an important factor to evaluate the drying shrinkage of cenmentitious materials. The mass loss which expressed as percentage of total sample mass change for AAMs with various DSG dosage is plotted in Fig. 6. In Fig. 6(a), it can be seen that AAS without gypsum shows the lowest mass loss in the first two weeks, although its drying shrinkage value is almost maximum. Adding DSG increases the mass loss of AAS mortar, which may be explained by the evaporation of a certain amount of free water absorbed inside the porous ettringite [20], while the mass loss of AAS with CDSG decreases after about 30 days. In the case of HAC mortar, the mass loss decreases when the content of gypsum is less than 15 %, while higher amounts of DSG result in increased mass loss. Consequently, there is no correlation between mass loss and drying shrinkage observed in both AAS and HAC mortars.

3.4. Autogenous shrinkage

The autogenous shrinkage measurements for various DSG-AAM mortars are presented in Fig. 7. It is evident that the autogenous shrinkage of both AAS and HAC mortars decreases with increasing DSG content. Specifically, the 56-day autogenous shrinkage of the AAS sample with DSG dosages of 5 %, 10 %, 15 %, and 20 % decreases by approximately 32.9 %, 43.7 %, 55.2 %, and 63.4 % respectively. AAS with CDSG exhibits higher autogenous shrinkage as compared to that with DSG. In Fig. 7(b), the 56 d autogenous shrinkage of HAC mortar reduces by approximately18.6 %, 47.5 %, 61.9 % and 70.3 % as the amount of DSG increases from 5 % to 20 %. In summary, incorporating DSG can mitigate the autogenous shrinkage of both AAS and HAC mortars, although to varying



Fig. 6. Mass loss of different AAM mortars.



Fig. 7. Autogenous shrinkage of different AAM mortars.

degrees. Autogenous shrinkage refers to macroscopic volume reduction primarily caused by self-desiccation resulting from hydration reactions: capillary pressure generated through self-desiccation is considered a crucial driving force for AAMs behavior, while other factors such as hydration product type, condensation, recombination of gel particles also play significant roles [12]. Previous studies



Fig. 8. Total porosity and pore structure of various AAM pastes.

have attributed drying shrinkage in AAMs containing gypsum to expansive ettringite formation or even portlandite and Na_2SO_4 presence. However, reasons for the influence of DSG on autogenous shrinkage in AAMs remain unexplored thus far. Therefore, it is necessary to conduct a systematic study on the shrinkage behavior of AAM-DSG via pore structure, hydration product, and micro-morphology.

3.5. Pore structure analysis

The porosity and pore structure in AAMs play a crucial role in its shrinkage performance, thus it is essential to investigate the total porosity and pore size distribution to comprehend the impact of DSG on AAM shrinkage. Fig. 8. illustrates the pore distribution and total porosity for 28-day age DSG-AAM pastes measured by mercury intrusion. The compressive strength of AAM is influenced by large pores and total porosity, while the distribution of pore structure affects shrinkage performance. It is obvious that the total porosity of AAS paste increases with an increase in DSG dosage from 5 % to 15 %, but starts decreasing at a dosage of 20 %, while the total porosity for HAC paste continue to increase as DSG dosage rises from 5 % to 20 %. Additionally, the type of DSG does not affect the total porosity. There exists a strong correlation between total porosity and compressive strength in both AAS and HAC pastes. However, the total porosity is negatively correlated with the drying shrinkage and autogenous shrinkage value of DSG-AAM pastes which needs further interpretation through analysis of pore size distribution. Pore structures are commonly categorized into four types based on their sizes [32,33]: gel nanopores (<10 nm), mesopores (10–50 nm), middle capillary pores (50–100 nm) and large pores (>100 nm). In Fig. 8(b), it can be observed that inclusion of DSG leads to an increased proportion of gel pores (<10 nm) within the AAM paste to varying extents, potentially indicating enhanced gel formation, however, this hypothesis requires verification through ¹H NMR, XRD and TG analyses. Some researchers have suggested that mesopores volume (10–50 nm) significantly influences shrinkage magnitude in AAMs, particularly drying shrinkage [17,34,35]. In this study, the inclusion of DSG improved the mesopores volume to varying degrees while reducing drying shrinkage and autogenous shrinkage, which appears to contradict previous findings. So further clarification is needed through pore distribution analysis.

The well-known mechanism of drying shrinkage for AAM includes capillary tension theory, surface tension force theory, and separation pressure theory [15,36]. In high humidity ranges above 50 %, the capillary tension has been recognized as the primary driving force of shrinkage at relative humidity (RH) above 50 %. Meanwhile, the surface tension force theory is applicable to explain shrinkage below 40 % RH. Since the RH in this study is about 60 %, so capillary tension theory is considered as the major mechanism to evaluate the shrinkage behavior. The capillary pressure can be calculated using Laplace's equation shown in Eq.3,

$$P_{cap} = \frac{2\gamma}{r} \tag{3}$$

Where γ represents the surface tension of the pore solution and r denotes the critical radius of the capillary meniscus. The surface tension of the pore solution inside these studied specimens is assumed to be similar due to consistent alkali equivalents[35,37], hence it is determined by meniscus radius which influences both capillary pressure and shrinkage magnitude. The results of pore size distribution are summarized in Fig. 9. It is obvious that the inclusion of DSG increases the capillary diameter of the AAS and HAC pastes to some extent, thereby diminishing their shrinkage value. In Fig. 9(a), AAS3 slurry exhibits the largest pore diameter during AAS pastes resulting in the lowest drying shrinkage values. Although the pore size of AAS1 is similar to that of AAS3, the pore size distribution of AAS1 is mainly concentrated at 10 nm ~ 30 nm, which is significantly larger than that of AAS3. This may explain why the drying shrinkage rate of AAS1 is greater than that of AAS3. Regarding HAC paste, there exists a positive correlation between DSG content and increased capillary diameter which explains why shrinking values continue to decrease with increasing DSG content in this paste. It is worth noting that AACMs with the same quantity of DSG or CDSG demonstrate a similar distribution of pore sizes. Nevertheless, the



Fig. 9. Pore size distribution of various AAM pastes.

shrinkage behavior of AAMs are determined not only by pore structure, but also hydration phase composition, gel characteristics and microstructure evolution. So the further analysis were conducted via ¹H NMR, XRD, TG and SEM-EDS to reveal the underlying reason of the effect of DSG on the shrinkage properties of AAM.

3.6. ¹H NMR relaxometry

Low-field ¹H NMR can determine the water state of cementitious materials by measuring the transverse relaxation time (T_2) of water without affecting the reaction, which facilitates monitoring the evolution of water status to characterize the early reaction process of cementitious systems [38]. Based on the T_2 distribution, the water state in fresh paste can be distinguished into gel interlayer water (0.01–0.1 ms), gel water (0.1–1 ms), capillary water (1–100 ms), and surface water (100–10000 ms) [39,40]. Fig. 10 displays the normalized T_2 distribution of studied pastes at 12 hours of hydration. AAS and HAC exhibit only gel water signals, while capillary water signals appear in the curves of AAS and HAC with DSG. With an increase in DSG content, the main peak occurring at 0.1–1.0 ms gradually shifts to higher T_2 values, becoming shorter and wider. This shift indicates that the inclusion of DSG causes a transformation from gel water to capillary water, thereby reducing the hydration degree and gel product amount, resulting in a relatively porous structure and lower compressive strength, which is consistent with the results of MIP results and strength tests finding. Compared with AAS paste, HAC paste shows a wider main peak and more presence of capillary water, indicating a lower hydration level. As for CDSG, the increased signal intensity and shorter T_2 distribution of HACD curve compared to that with HAC1 imply that CDSG can promote the reaction degree to some extent compared to DSG. Another finding was that there was no gel interlayer water signal in all sample curves, indicating that no crystallization products were formed within 12 hours of hydration.

The evolution of the normalized T_2 distribution of various DSG-AAM pastes within 24 h (see Fig. 11) was examined to further investigate the influence of DSG on water state shift in the studied pastes. As hydration progresses, the T_2 distribution for AAS and HAC shifts from 1 to 10 ms to 0.1–1 ms, indicating a transition from capillary water to gel water and significant generation of gel products. Upon addition of DSG, the capillary water signal starts appearing on the T_2 distribution curve of the specimens under study, with its intensity becoming more pronounced as DSG content increases. This suggests a slower reaction rate and formation of a porous flocculent structure. Notably, after 6 hours of hydration, both HAC and AAS exhibit diminished signal intensity and broader T_2 distributions, indicating water consumption and an increase in pore diameter within the formed structure. In comparison with the HAC paste, AAS displays a higher and sharper main peak in its T_2 distribution, suggesting a faster reaction rate and increased hydration products [41].

The normalized T_2 distribution diagram illustrates the variation in total water content within the slurry, while it is also essential to calculate the water content within specific intervals (ω i) for a deeper understanding of the influence of water status evolution on DSG-AAMs hydration. The ω ican be determined using Eq.(4) [42]:

$$\omega_{i} = \left(\int_{T_{i}}^{T_{f}} I_{T_{2}} d \lg T_{2} / \int_{0.01}^{10000} I_{T_{2}} d \lg T_{2}\right) * \omega / m_{s}$$
(4)

where T_i and T_f represent the transverse relaxation time at the beginning and end of the specified interval, respectively; ω denotes the total water content in the sample, and m_s is the mass of paste sample. Water with a signal ranging from 0.01 to 1 ms is attributed to immovable water, whereas water with a signal range between 1 and 100 ms refers to mobile water. The calculated results based on normalized T_2 distribution are presented in Fig. 12. The increase in immovable water content and decrease in mobile water during the hydration reaction were observed in both AAS and HAC pastes, with the addition of DSG causing a delay in this trend. Moreover, as the content of DSG increased, the change trend became more moderate. For instance, while significant changes in water status were observed within the first 10 minutes of hydration for AAS and HAC pastes, it took 3 hours for AAS4 and 1 hour for HAC4 to transition from mobile water to immovable water. Consequently, AAMs containing DSG exhibited slower hydration rates leading to fewer hydration products and a porous microstructure. In comparison to AAS, the HAC paste had lower total water content and slower transitions between different states of water. Additionally, the conversion rate from immovable water to mobile water was slower in AAS with CDSG compared to that with an equivalent amount of DSG, however, this relationship was reversed in the HAC paste. These findings suggest that CDSG has a lower hydration reaction rate in AAS pastes than it does in HAC pastes.



Fig. 10. Normalized T₂ distribution of various AAM pastes (12 h).



Fig. 11. Normalized T2 distribution of various AAM pastes at different ages.



Fig. 12. The evolution of water content in AAM pastes.

3.7. XRD analysis

Previous studies have demonstrated that the inclusion of gypsum in AAM can partially compensate for shrinkage by facilitating the formation of expansive crystals, such as ettringite and portlandite [18–20,43]. Therefore, XRD analysis was conducted to determine the extent of crystal formation in the DSG-AAM paste. The XRD patterns for DSG-AAS pastes after 3-day and 28-day of curing are presented in Fig. 13. It is evident from these patterns that the introduction of DSG results in the development of crystalline phases, including ettringite (PDF# 41–1451), hydrotalcite (PDF# 41–1428),gehlenite (PDF# 35–0755) and portlandite (PDF# 44–1481), which aligns with previous research findings[20,43]. However, it should be noted that the diffraction peaks associated with these crystal products are relatively small and weak and do not exhibit any significant increase over time. Additionally, an increase in unreacted DSG content is observed with higher dosages, indicating a decrease in reaction participation when using increased amounts of DSG. In contrast to regular DSG, CDSG does not promote crystal product formation within AAS pastes. The broad and diffuse peak around 30° 20 attributed to amorphous gel products and calcite (PDF# 05–0586) becomes sharper as the increasing DSG, this suggests an enhanced degree of crystallization for hydration products.

Similar to AAS pastes, HAC pastes also generate certain crystalline hydration products (e.g., ettringite, portlandite, gehlenite, and hydrotalcite) [44] upon incorporating DSG (Fig. 14). The intensity of diffraction peaks associated with these crystalline products increases proportionally with increasing amounts of DSG but does not show any further increment over curing time. The presence of these crystalline reactants can mitigate shrinkage values within HAC pastes to some extent. Conversely, no diffraction peaks corresponding to crystalline products are observed in the XRD patterns for HAC pastes with CDSG. In summary, the introduction of CDSG does not appear to affect the phase composition of hydration products for AAM. This may be due to the limitations of XRD technology in comprehensive detection.

The semi-quantitative XRD analysis of the DSG-AAM paste based on Whole Pattern Fitting and Rietveld Refinement is shown in Table 3. The addition of DSG is observed to result in an increase in ettringite, hydrotalcite, and Portlandite content. ¹H NMR analysis reveals a decrease in gel product formation upon the addition of DSG, consequently leading to a reduction in the amount of crystalline C-S-H (PDF# 41–0035) as indicated by XRD analysis, particularly evident in the 28-day sample. The presence of more unreacted gypsum in the slurry and the increased levels of C₂S (PDF# 33–0302) and C₃S (PDF# 16–0406) in the HAC paste suggest a reduction in the extent of AAM reactions upon addition of DSG.

The XRD results reveal that the addition of DSG leads to the formation of crystalline phases such as ettringite, hydrotalcite, and portlandite in the AAM paste. Additionally, it enhances the degree of crystallization of hydration products, thereby contributing to a higher ratio of crystalline/gel phases. This phenomenon can be considered as one factor mitigating the shrinkage value of AAM mortar by DSG. For hydrate phase analysis, XRD is typically combined with TG-DTG to ensure the accuracy of phase identification.

3.8. TG-DTG analysis

It is widely acknowledged that the determination of chemically-bound water quantity can provide valuable insights into hydration products in the AAM system [45]. In order to accurately quantify the amount of chemically-bound water in hydrated slurry, thermogravimetry (TG) is employed to monitor its consumption in the AAM-DSG paste, thereby facilitating analysis of both reaction products and processes within the system. The TG-DTG curves for pastes studied at 3-day ages are presented in Fig. 15. The significant peaks observed between 100 and 120 °C primarily result from the decomposition of C-(A)-S-H gels and AFt [46]. Incorporation of DSG



Fig. 13. XRD patterns for DSG-AAS pastes at 3 d and 28 d ages.



Fig. 14. XRD patterns for DSG-HAC pastes at 3 d and 28 d ages.

Table 3XRD quantitative analysis of DSG-AAM pastes at 3 d and 28 d ages.

System		C-S-H	Bassanite	C_2S	C_3S	Gehlenite	Gypsum	Ettringite	Portlandite	Hydrotalcite	Calcite
3d	AAS	68.8	0	0	0	16.1	0	0	0.8	0.8	13.5
	AAS1	56.5	0	0	0	18.7	6.3	2.0	4.5	2.2	9.8
	AAS4	45.3	0	0	0	20.7	13.5	7.5	2.2	4.0	6.8
	AASD	54.4	3.6	0	0	21.3	3.1	1.2	2.1	2.3	12.0
	HAC	55.8	0	7.7	11.0	8.0	0	0	1.2	2.1	14.2
	HAC1	46.2	0	6.6	8.2	9.6	4.9	1.6	6.2	3.0	13.7
	HAC4	39.6	0	4.9	4.5	11.5	7.8	9.9	2.0	5.6	14.2
	HACD	49.4	2.3	6.0	8.4	6.5	2.4	1.4	5.2	3.8	14.6
28d	AAS	59.4	0	0	0	19.9	0	0	2.9	2.0	15.8
	AAS1	50.1	0	0	0	21.3	3.6	2.8	6.4	4.8	11.0
	AAS4	42.7	0	0	0	23.5	9.9	8.2	1.2	7.3	7.2
	AASD	48.9	3.6	0	0	16.6	3.9	2.3	4.3	4.4	16.0
	HAC	48.4	0	8.0	9.4	10.0	0	0	3.8	2.9	17.5
	HAC1	42.0	0	7.1	7.0	11.4	2.4	3.2	7.7	2.1	17.1
	HAC4	37.0	0	4.3	2.0	13.5	5.0	11.0	1.5	5.0	20.7
	HACD	45.0	2.8	6.5	4.0	9.8	2.0	2.3	4.8	3.8	19.0



Fig. 15. TG-DTG curves for various AAM pastes at 3 d ages.

reduces these peaks in both AAS and HAC systems, indicating a decrease in hydration degree and product formation, which is consistent with the ¹H NMR results. The appearance of peaks around 140°Ccan be attributed to unreacted DSG, with their relationship to DSG content consistent with XRD results. CDSG exhibits minimal peaks at 100–120 °Cand no unreacted gypsum according to DTG curve analysis. Mass loss occurring at approximately 340°Cand 440°Ccorresponds respectively to dehydration of hydrotalcite and portlandite [47,48], which aligns with XRD findings as well. Peaks associated with paste carbonation due to CaCO₃ appear between 600 and 800 °C [49]. The main reason for the presence of CaCO₃ in the samples lies in the chemical reaction of DSG in alkali solution to produce Ca(OH)₂, and the carbonation of Ca(OH)₂ in air generates CaCO₃[20,24]. On the oether hand, the detection of CaCO₃ could be due to the carbonation of C-S-H, which is common in AAMs with slag. At an age of 28 days, mass loss increases for both alkali-activated systems as shown in Fig. 16, indicating an increase in product quantity through hydration reactions. There is little change observed regarding types of hydration products compared to those cured for only 3 days except for a reduction or even absence of peak intensity related to portlandite and hydrotalcite, especially noticeable within the AAS paste. It is also found that the peaks intensity of gel in AAS with DSG is greater than that of AAS without gypsum, but the gel amount decreased observed in ¹H NMR analysis, hence indicating more AFt generated with increasing of DSG content. The incorporation of DSG leads to a reduction in chemical-bound water, indicating a decrease in reaction degree [50].

Table 4 lists the weight loss of some representative samples. It is evident that the product gels of HAC and AAS gradually decreases with the addition of DSG, which is consistent with the results of ¹H NMR. The reduction of product gel due to the increase of DSG content in AAMs is one of the main reasons for the decrease of its mechanical performance. It can also be seen from Table 4 that the inclusion of DSG increases the crystal content in HAC and AAS, and the crystal content increases with the increase of DSG, which again confirms that the introduction of crystalline products alleviates the drying shrinkage of AAMs with DSG.

3.9. SEM-EDS analysis

Due to the significance of gel properties and microstructure evolution on shrinkage properties, SEM-EDS was employed to investigate the micro-morphology and composition of hydration products. The 3d and 28 d SEM images for the DSG-AAM paste are displayed in Fig. 17 and Fig. 18, respectively. It can be observed that both AAS and HAC exhibit homogeneous and dense matrices composed of numerous hydration products along with a small amount of unreacted raw materials. With the addition of DSG, the matrix becomes looser and is accompanied by crystalline products such as ettringite, hydrotalcite, and portlandite as reported previously [20, 43]. This porous structure contributes to increased porosity and decreased compressive strength while the formation of crystalline hydration products mitigates shrinkage values in DSG-AAM systems. Compared to AAS systems, HAC systems display higher porosity along with more crystalline products leading to lower strength and shrinkage values. In terms of DSG type, there is no discernible difference in microstructure compactness between DSG-AAM and CDSG-AAM at equivalent gypsum dosages. After comparing the 3-day and 28-day SEM images, it is apparent that the microstructure of AAS and HAC becomes denser as curing age. The inclusion of DSG results in a notable increase in the quantity of ettringite hydration products over time. Additionally, needle-rod crystals are visually identifiable in CDSG-AAM matrix but not detectable by XRD analysis.

As mentioned in the previous section, the Ca/Si ratio of the C-(A)-S-H gel is considered to be a crucial factor affecting the shrinkage of the cementitious material [11,51], meanwhile the Al/Si ratio is usually positively correlated with the degree of polymerization for C-(A)-S-H gel. Therefore, the Ca/Si ratio and Al/Si ratio of the gel products in studied specimens were determined by combining EDS surface spectrum and point spectrum analysis, and are presented in Table 5. It is observed that Ca/Si ratio of gels in AAM paste with DSG increases to vary degrees. The reason may be that DSG provides more Ca²⁺ ions to the system and then improves the Ca/Si ratio of the gel. Gels with higher Ca/Si ratios generally exhibit reduced shrinkage, attributed to the tendency of calcium to form an ordered structure and silicon to form an amorphous structure[10]. Gels in HAC paste possesses a higher Ca/Si ratio compared to AAS paste as reported in previous research, so HAC paste exhibit lower shrinkage than AAS paste[10]. There is a relatively well correlation between drying shrinkage and Ca/Si ratio of gel phase in this study. Table 5 also demonstrates that the inclusion of DSG results in a lower Al/Si ratio gel phase, indicating a decrease in the polymerization degree of C-A-S-H, thereby leading to prolonged setting time and reduced compressive strength.

4. Discussion

4.1. Action mechanism analysis

The findings from the previous part of this study demonstrate that the inclusion of DSG can alleviate the shrinkage of AAS and HAC systems, especially autogenous shrinkage. During the early stages of hydration reaction, DSG exhibits a noticeable retarding effect on setting of AAMs. The ¹H NMR analysis reveals that DSG converts gel water in the slurry into capillary water, indicating reduced hydration levels which result in a lower amount of gel products and a relatively porous structure. The underlying mechanism is as follows: during dissolution, DSG releases SO₄ ²⁻ and Ca ²⁺ ions; as the reaction progresses, a significant amount of C-(A)-S-H gel products begin to form. However, due to its large specific surface area and negative charge resulting from deprotonation of Si-OH groups, these SO₄ ²⁻ and Ca ²⁺ ions are easily adsorbed onto the surface or pore walls of C-(A)-S-H gel [52]. This adsorption effect hinders gel polymerization by occupying space, thereby reducing surface tension and ultimately decreasing shrinkage values[23,53]. With an increase in DSG content, more SO₄ ²⁻ and Ca ²⁺ ions are absorbed and occupy larger spaces within the paste, further impacting gel polymerization processes and gradually reducing shrinkage values. This explains why DSG affects AAM shrinkage during early stages. On the other hand, SO₄ ²⁻ ions were temporarily adsorbed within the gel matrix, resulting in a lack of ettringite formation during



Fig. 16. TG-DTG curves for various AAM pastes at 28 d ages.

Table 4

The weight losses of different phases in AAS and HAC pastes.

Weight loss (%)		Gel	AFt (Ettringite)	Gypsum	Hydrotalcite	Portlandite	Calcite
3d	AAS	6.65	0	0	0.88	0.94	4.06
	AAS1	6.45	0.62	1.49	0.74	1.24	1.86
	AAS4	4.59	1.81	2.18	0.73	1.45	1.33
	AASD	4.98	0.40	1.29	0.70	0.91	1.69
	HAC	7.68	0	0	1.10	1.34	3.12
	HAC1	6.96	0.85	1.42	0.85	1.85	2.27
	HAC4	5.12	1.83	1.58	0.98	0.49	2.19
	HACD	4.95	0.44	0.99	0.77	1.54	2.31
28d	AAS	10.14	0	0	1.09	1.25	3.12
	AAS1	8.53	0.63	0.95	1.11	1.89	2.68
	AAS4	6.24	2.49	2.34	0.62	1.72	2.18
	AASD	7.54	0.73	0.58	1.02	1.16	3.48
	HAC	10.85	0	0	1.16	1.49	2.97
	HAC1	8.67	1.19	0.85	1.36	2.21	2.72
	HAC4	6.40	2.49	1.25	1.87	0.62	2.96
	HACD	6.62	0.88	1.18	1.32	1.47	3.23



Fig. 17. Microtopography of DSG-AAM pastes for 3 d curing.



Fig. 18. Microtopography of DSG-AAM pastes for 28 d curing.

Table 5Ca/Si ratio and Al/Si ratio of the studied gels at 3 d and 28 d.

Sample No.	3 d		28 d		
	Ca/Si	Al/Si	Ca/Si	Al/Si	
AAS	0.95	0.36	1.02	0.39	
AAS1	0.99	0.39	1.15	0.48	
AAS2	1.00	0.26	1.21	0.62	
AAS3	1.10	0.21	1.10	0.26	
AAS4	1.34	0.61	1.53	0.29	
AASD	1.14	0.31	1.10	0.26	
HAC	1.06	0.39	1.05	0.32	
HAC1	1.26	0.53	1.14	0.29	
HAC2	1.30	0.23	1.21	0.25	
HAC3	1.41	0.21	1.27	0.39	
HAC4	1.33	0.36	1.37	0.54	
HACD	1.71	0.29	1.61	0.60	

the initial stages of hydration reaction. Consequently, the ¹H NMR results indicated that no crystal water-containing products were formed within 24 hours of hydration. As the hydration reaction progressed, more DSG dissolved and released additional SO_4^{-2} ions, leading to gradual formation of needle-like ettringite crystals within the matrix along with other crystalline phases such as gehlenite and hydrotalcite. These crystal products exhibited excellent volume stability and contributed to reducing shrinkage in AAMs to some extent. Furthermore, the high Ca/Si ratio C-(A)-S-H gel formed due to calcium provided by DSG also helped mitigate shrinkage in AAMs. Finally, from a microstructural perspective, incorporating DSG resulted in an increase in total porosity and consequently varying degrees of strength reduction. Based on MIP results, it can be observed that this increase in porosity primarily stemmed from an augmentation in capillary pores and certain gel pores. Furthermore, the presence of a higher content of DSG led to an increase in capillary pore diameter, resulting in a subsequent decrease in capillary pressure according to the Laplace equation and ultimately contributing to a reduction in mortar shrinkage value. Moreover, unreacted DSG could potentially occupy larger pores, thereby playing a role in mitigating AAMS shrinkage.

Regarding the interaction between DSG and the activator, the crystal phase of $Ca(OH)_2$ is first formed during the dissolution of DSG in the alkaline solution. Subsequently, the released SO_4^{2-} ions react with the Ca and Al components from the slag to form the crystal phase of ettringite, accompanied by the precipitation of dihydrate gypsum. These crystal phases not only serve as a structural framework but also contribute to micro-expansion properties. The ettringite crystals, in particular, help compensate for shrinkage. Furthermore, a higher gel crystallinity ratio can mitigate the long-term shrinkage of AAMs, effectively reducing the risk of late-stage cracking. This, in turn, decreases the infiltration of water and corrosive substances into the matrix, ultimately enhancing the long-term durability of AAMs.

4.2. Differences in the effects of DSG and CDSG

The components of DSG and CDSG are shown in Fig. 1(b). The main component of CDSG is $Ca_2SO_4 \cdot 0.5H_2O$, while the primary component of DSG is $Ca_2SO_4 \cdot 2H_2O$. The dissolution rate and solubility of $Ca_2SO_4 \cdot 0.5H_2O$ are generally higher than those of $Ca_2SO_4 \cdot 2H_2O$, resulting in a greater concentration of SO_4^{-2-} and Ca^{2+} ions in the reaction system. Based on the aforementioned reaction mechanism, AAMs containing CDSG exhibit a longer setting time and lower compressive strength compared to those with DSG. However, the drying shrinkage mitigation effect of CDSG in AAS mortar was found to be superior to that of DSG in HAC mortar at equivalent dosages, which can be attributed to the slightly higher crystal phase content, as shown in Table 3. Interestingly, while CDSG demonstrated a more significant reduction in autogenous shrinkage in HAC mortar, it showed the opposite effect on drying shrinkage. The type of DSG does not appear to significantly influence the phase composition or microstructure of hydration products in AAMs. In conclusion, CDSG does not offer a more pronounced reduction in shrinkage for AAMs compared to DSG. Therefore, DSG is more suitable for addressing shrinkage issues in AAMs due to its lower energy consumption and minimal impact on the mechanical properties of AAMs.

4.3. Comparative analysis of DSG and other shrinkage-reducing agents

DSG can help mitigate the shrinkage problem of AAMs to some extent, particularly in terms of autogenous shrinkage. As an industrial byproduct, DSG offers advantages such as low cost, low energy consumption, and low carbon footprint compared to other commercial shrinkage-reducing agents. However, the shrinkage-reduction effect of DSG is slightly lower than that of commercial agents, and it results in a marginally greater strength loss. Future research could focus on optimizing the DSG content to achieve better shrinkage reduction.

5. Conclusions

The impact of DSG on the shrinkage behavior of AAS and HAC systems was evaluated and compared with CDSG, encompassing the hydration process, mechanical properties, and drying/autogenous shrinkage. The hydration process and product, pore distribution, and microstructure evolution were monitored using ¹H NMR, XRD, TG-DTG, MIP, and SEM-EDS. Based on the aforementioned analysis results, the primary conclusions can be achieved as follows:

- The incorporation of DSG will show hydration reaction of AAMs and reduce hydration product formation, resulting in a prolonged setting time and decreased strength, particularly at early age.
- The effectiveness of DSG mitigating drying shrinkage depends on AAM type. This study, in the HAC mortar, the drying shrinkage consistently decreased with increasing DSG content; however, an content of 15 % DSG demonstrated the minimum drying shrinkage value in the AAS system. Furthermore, the drying shrinking mitigation effect of CDSG in AAS mortar was found to be superior to that of DSG observed in HAC mortar at equivalent dosage. Mass loss did not exhibit a strong correlation with drying shrinkage in this study.
- Incorporating DSG significantly reduces autogenous shrinkage of AAMs. There is a positive correlation between DSG content and autogenous shrinkage observed in both the AAS and HAC systems; however, a greater reduction was observed in the HAC mortar. Additionally, CDSG demonstrated a higher reduction effect on autogenous shrinkage specifically within the HAC mortar, contrary to its impact on drying shrinkage.
- DSG can impede the polymerization process of AAMs, leading to a decrease in reaction rate and subsequently resulting in reduced gel products and porous structure formation. Furthermore, it facilitates the generation of crystalline products and higher Ca/Si of gel (amorphous C-A-S-H) phase, thereby enhancing the volume stability of AAMs. An increase in capillary pore diameter reduces capillary pressure as per Laplace equation, together contributing to a reduction of shrinkage.

CRediT authorship contribution statement

Xue Lili: Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. Ni Zhenkun: Writing – original draft, Software, Investigation, Formal analysis. Zhou Zhengning: Methodology, Formal analysis, Data curation. Zhang Zuhua: Supervision, Funding acquisition, Conceptualization. Xiong Houren: Supervision, Methodology, Conceptualization. Wang Hao: Supervision, Conceptualization. Zhuge Xifeng: Software, Data curation. Liu Hongfei: Supervision, Methodology, Conceptualization.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Zuhua Zhang reports was provided by National Natural Science Foundation of China. Lili Xue reports financial support was provided by Science and technology project of Jiaxing City, Zhejiang Province. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The data that has been used is confidential.

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