INTRODUCTION

The balance between the reaction of aluminate-containing clinker phases (C₃A, C₄AF) and sulfates is one of the crucial factors for the hydration of Portland cement. Based on studies of the impact of sodium, potassium, and calcium sulfates, Tang and Gartner¹ proposed that both the chemical and physical forms of the sulfate sources significantly influence the initial consumption of the aluminate-containing clinker phases. The stiffening and initial setting processes of cementitious materials are commonly regulated by the addition of calcium sulfates (including gypsum, hemihydrate/bassanite, and anhydrite, the so-called “sulfate carriers” or “set regulators”) during the grinding of the clinker to avoid a fast reaction of the aluminate-containing clinker phases when they come into contact with water. The general reaction processes are independent of the kind of sulfate carrier used, but the differences in solubility and dissolution rate of the sulfate carriers can substantially influence the macroscopic properties of cementitious materials, such as the development of fluidity over time and the initial as well as the final setting time of the cement.² Three On the microscopic level, the use of

Impact of triethanolamine on the sulfate balance of Portland cements with mixed sulfate carriers

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Abstract

The differences between the hydration of Portland cements with single and with mixed sulfate carriers in the presence of triethanolamine (TEA) were investigated, and possible mechanisms were proposed. Without TEA, cements with different types of sulfate carriers (gypsum, hemihydrate, anhydrite, and mixture of these) have a comparable hydration process at the same molar amount of calcium sulfate. At a TEA dosage of 0.5 wt.%, the sample with a mixture of three sulfate carriers shows substantially stronger retardation of the C₃S (This publication uses the cement chemist notation: C₃S = Ca₃SiO₅, C₂S = Ca₂SiO₄, C₃A = Ca₃Al₂O₆, C₄AF = Ca₂(Al, Fe)₂O₇.) hydration than the cements with only one of these sulfate carriers, which is likely caused by the rapid formation of ettringite and the fast depletion of all sulfate carriers. These effects indicate that TEA influences the balance of sulfate carriers with aluminate-containing clinker phases. On the one hand, TEA can disturb the original sulfate balance due to the accelerated dissolution of aluminate-containing clinker phases, especially C₄AF. On the other hand, these effects are closely related to the types and amounts of the sulfate carriers in the cement. A higher amount of sulfate carriers can minimize the TEA-related retardation of the C₃S hydration, and hemihydrate shows the strongest impact at the same calcium sulfate quantity.

KEYWORDS

aluminates, calcium silicate hydrate, hydration, Portland cement, triethanolamine (TEA)
hemihydrate can slightly accelerate the silicate reaction, and more ettringite can be formed in the early hydration. Pourchet et al. studied the hydration of C_3A with various amounts of gypsum, hemihydrate, or mixtures of the two. It was found that the hydration of C_3A and the initial formation of AFm phases (equivalents to the minerals of the hydrocalumite-kuzelite group) or ettringite (AFt) depend on the degree of super-saturation in the solution. The use of hemihydrate can prevent the initial formation of AFm by increasing the nucleation frequency of ettringite.

On the other hand, the alumin ate hydration can be significantly modified by the addition of chemical admixtures such as superplasticizers. Triethanolamine (TEA) is often used as a grinding agent or setting modifier in the production and application of cementitious materials. The addition of TEA can accelerate the initial reaction of the alumin ate-containing clinker phases, including C_3A and especially C_4AF, and can retard the main silicate reaction. The retarding effect of TEA on the main silicate reaction seems to be dominated by the accelerated reaction of alumin ate-containing clinker phases rather than the direct interaction of TEA with the silicate phases. Due to the interactions of multiple phases in cements and the variety of effects of TEA on these phases, the impact of TEA on the setting of cement paste shows a complex dependence on the dosage.

Recent studies have revealed that TEA affects not only the hydration of the main clinker phases but also the dissolution of sulfate carriers. Recchi et al. reported a substantial influence of the type and quantity of single sulfate carriers on the workability and compressive strength of TEA-added mortars. However, a deeper understanding of the basic mechanisms is still missing. Consequently, a systematic study about the impact of different sulfate carriers on the hydration of Portland cement with TEA should be conducted. Such a study should furthermore include mixtures of sulfate carriers as most Portland cements contain a mixture of several sulfate carriers. The possible differences between the hydration of cements with a single type of sulfate carrier and with mixed sulfate carriers should be explained.

To answer these questions, the hydration processes of artificial cements (ArCs) made from Portland cement clinker and different amounts and proportions of three sulfate carriers (gypsum, hemihydrate, and anhydrite) were examined with as well as without the addition of TEA in the current study. Isothermal conduction calorimetry, elemental analysis of extracted pore solutions by inductively coupled plasma optical emission spectrometry (ICP-OES), in-situ X-ray diffraction (XRD), thermogravimetry (TG), and low-vacuum scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) were utilized. The presented results provide a deep understanding of the interaction of different sulfate carriers with TEA and the corresponding effect on the sulfate balance and cement hydration. These new insights are essential to understand why there is a maximum quantity of TEA, beyond which adverse effects like flash setting and/or serve retardation of the silicate reaction occur and why this threshold is strongly varying between different Portland cements. Such knowledge will help to optimize the interaction of TEA and other admixtures with cements, for example, to control the setting and hardening process, and could potentially facilitate the development of recent applications of Portland cement. In particular, a precisely timed acceleration will be a great advantage in digital fabrication of concrete.

2. MATERIALS AND METHODS

2.1. Materials

A ground Portland cement clinker (OPTERRA Zement GmbH) was used in this study. For comparison, the commercial ordinary Portland cement (OPC, CEM I 52.5 R) based on this clinker (different batch of production) was additionally examined. The clinker and the OPC were produced on an industrial scale. The particle size distributions of clinker and OPC obtained by laser diffraction (Mastersizer 2000, Malvern Panalytical) and the specific surface areas measured by the Blaine method are shown in Figure S1 and Table S1. The chemical compositions of the clinker and OPC were examined by X-ray fluorescence (XRF, WD-RFA PW 2400, Philips), and the mineralogical compositions were refined using the Rietveld method based on XRD (Empyrean and Highscore Plus, Panalytical). The results are shown in Table 1.

Natural anhydrite and flue gas desulfurization (FGD) gypsum used in the production of the OPC were obtained and ground (Pulverset 5, Fritsch GmbH). Hemihydrate was produced from ground FGD gypsum by heating it for 3 weeks at 105°C in a muffle furnace (this long time and low temperature were needed to achieve the full conversion of gypsum without the formation of anhydrite III). The chemical compositions of these sulfate carriers were examined by XRF (Axios, Panalytical), and the mineralogical compositions were refined using the Rietveld method based on XRD (Empyrean and Highscore Plus, Panalytical). These results are shown in Table 1, and all structure codes used for evaluation of XRD, including the Rietveld refinements, are given in Table S2. The results of the Rietveld refinements on the sulfate carriers were verified by the weight losses observed in the thermogravimetric analysis. These three sulfate carriers were used for the preparation of ArCs and will be abbreviated in the following as AH, GS, and HH, respectively, while the mineralogical phases will be referred to as anhydrite, gypsum, and hemihydrate, respectively.

To verify the effects found, ArCs were prepared containing gypsum, hemihydrate, and/or anhydrite originating form
The gypsum was used as received, and hemihydrate was produced as described before. Anhydrite was made by annealing the gypsum in a muffle furnace at 550°C for 5 h, followed by 775°C for 48 h. These ARCs were in their calcium sulfate contents equivalent to GS/2.88, HH/2.88, AH/2.88, and MX/2.88 and named as GS_Chem/2.88, HH_Chem/2.88, AH_Chem/2.88, and MX_Chem/2.88, respectively (Table 2).

The particle size distributions of the industrial sulfate carriers and the chemical calcium sulfates were measured by laser diffraction (Mastersizer 2000, Malvern Panalytical; Figure S1). In all experiments, analytical grade TEA (VWR Chemicals) and double-deionized water were utilized.

### 2.2 | ARC preparation

ARCs with various types, amounts, and proportions of industrial sulfate carriers (or chemical calcium sulfates) were produced to evaluate the impact of these differences on the hydration of cement pastes with TEA addition. Dry ARCs were prepared from the ground Portland cement clinker and the sulfate carriers by mixing in an overhead shaker (REAX 20/12, Heidolph Instruments), as given in Table 2. To achieve the SO₃ levels given in Table 2, the effective content of SO₃ in each sulfate carrier—depending on the type of calcium sulfate (hydrate) and the amount of minor phases—was taken into consideration. An overall amount of 2.88 wt.% added SO₃ was found to be the optimum value based on the cumulative heat of hydration till 1 day in isothermal calorimetry when using HH as the sulfate carrier. Samples with other quantities of SO₃ were also prepared to evaluate the impact of altered contents and shares of sulfate carriers on the effect of TEA. The specific surface areas of representative and the particle size distributions of all samples are shown in Table S1 and Figure S1, respectively. The powders were rested for at least 1 day, before they were used for the following experiments.

### 2.3 | Cement paste experiments

Cement pastes were prepared from the aforementioned ARC powders by adding water or water–TEA solutions. For chemical gypsum (Merck, purity 99%).
water–TEA solutions, TEA was given into water at dosages of 0.1 and 0.5 wt.% (with respect to ArC or OPC). These solutions were rested 1 day before the use in paste preparation. The water-to-cement ratio (w/c) was 0.41 in the calorimetry, XRD, TG, and SEM-EDS. For the extraction of pore solution, the water-to-cement ratio was increased to 0.7, as the fast stiffening of the sample AH/2.88 with 0.5 wt.% TEA prevented the extraction at w/c = 0.41. For all experiments, samples as well as devices were conditioned to 20°C. Pastes of ArCs and OPC were prepared by vortex mixing for 1 min. For conduction calorimetry, an MC-CAL/100P (C3 Prozess- und Analysentechnik GmbH) was used. Each experiment was performed with 2.3 g dry ArC powder and the corresponding water amount of 0.943 g. Due to the applied external mixing, the heat flow of the first hour was excluded from the calculation of the cumulative heat. The cumulative heat and heat flow were normalized using the weight of ArC/OPC.

The pore solutions of the pastes were collected after 5 min of undisturbed hydration by centrifugation at 3317 g for 10 min. The obtained supernatant was filtered (pore diameter 0.45 μm) and acidified with HNO₃ (2 wt.%) with a volume ratio of acid to supernatant of 2:1. ICP-OES (IRIS Intrepid II XSP, Thermo Fisher) was used to quantify the concentrations of Ca, Fe, Al, Si, Na, and K. The pH was calculated by the computer program PHREEQC based on the charge balance.

In situ XRD was performed with a Bragg–Brentano diffractometer (Empyrean, Panalytical) on a cooling stage. The Cu Kα radiation (40 kV, 40 mA) was filtered using Ni and collected with a PiXcel™ detector. Each paste was poured into the sample holder and covered by a polyimide foil. The first measurement started at 3.5 min after the beginning of mixing. Each scan (continuous mode, 8°–35° 2θ) took 7.5 min. The evaluation was done by comparing the intensities of the characteristic phase reflexes determined with the software HighScore Plus 4.8 (Panalytical). The comparison of characteristic diffractions based on the crystal structures (Table S2) was chosen, as it gives adequate results in the scope of this study.

Low-vacuum SEM (GeminiSEM500 Nano VP, ZEISS) and TG (TG; TG2 09 F3 Tarsus, Netzsch) were performed on selected samples with or without 0.5 wt.% of TEA after 5 min of hydration. The hydration of the samples was stopped by liquid nitrogen. Thereafter, the samples were dried under vacuum for 3 days. The SEM was operated at a gas pressure of 150 Pa and a voltage of 15 kV. Secondary electrons (SE) were detected to obtain micrographs of the particle topography. Additionally, EDS was performed to characterize the precipitates more in detail. For TG, approximately 10 mg of each sample was heated at 10 K/min to 850°C in a nitrogen atmosphere with a flow rate of 40 ml/min.

### RESULTS

#### 3.1 Hydration of OPC and ArCs with single and mixed sulfate carriers

Figure 1A,B shows the impact of TEA on the heat development of the commercial OPC and several ArCs with different sulfate carriers. Without TEA, there are only minor

| Table 2 Amount of added SO₃ by industrial sulfate carriers or chemical calcium sulfates in the ArCs (wt.% with respect to Portland cement clinker) |
|-----------------|-----------------|-----------------|-----------------|
| Total added SO₃| Added by GS     | Added by HH     | Added by AH     |
| MX/1.44         | 1.44            | 0.48            | 0.48            | 0.48            |
| GS/2.88         | 2.88            | 2.88            | —               | —               |
| HH/2.88         | 2.88            | —               | 2.88            | —               |
| AH/2.88         | 2.88            | —               | —               | 2.88            |
| MX/2.88         | 2.88            | 0.96            | 0.96            | 0.96            |
| MX_GS/4.32      | 4.32            | 2.40            | 0.96            | 0.96            |
| MX_HH/4.32      | 4.32            | 0.96            | 2.40            | 0.96            |
| MX_AH/4.32      | 4.32            | 0.96            | 0.96            | 2.40            |
| MX/5.76         | 5.76            | 1.92            | 1.92            | 1.92            |

| Total added SO₃| Added by gypsum | Added by hemihydrate | Added by anhydrite |
|----------------|-----------------|----------------------|-------------------|
| GS_Chem/2.88   | 2.88            | —                    | —                 |
| HH_Chem/2.88   | 2.88            | —                    | 2.88              |
| AH_Chem/2.88   | 2.88            | —                    | —                 |
| MX_Chem/2.88   | 2.88            | 0.96                 | 0.96              |

Abbreviation: ArCs, artificial cements.
differences in the hydration of OPC and the ArCs. The addition of 0.1 wt.% TEA leads to a slight delay of the main hydration peak in all samples, but the principal behavior of the five samples is still comparable. The height of the main hydration peak is slightly increased for the OPC, whereas the heights for the ArC pastes are nearly unchanged. Nevertheless, a strong diversification occurs upon the addition of 0.5 wt.% TEA. At this dosage, the main hydration peaks of all samples are further delayed but to a considerably different extent. The strongest delay can be recognized for the ArC with the mixed sulfate carriers in a molar ratio of 1:1:1 (MX/2.88), and the OPC shows the main hydration at a time comparable to MX/2.88. Furthermore, the heat maxima are substantially decreased in both samples. The three ArCs with only one sulfate carrier experience a more moderate delay. The maxima of the main peaks of these three ArCs are higher than that with the mixed sulfate carriers but differ from each other. The main peak of GS/2.88 appears slightly deformed. However, the most crucial observation is that the ArC containing a mixture of sulfate carriers (MX/2.88, Table 2) and the commercial OPC (which also contains all three sulfate carriers, Table 1) show a substantially more prolonged induction period than the ArCs with only one sulfate carrier.

As already mentioned, the commercial OPC and the clinker used in this study are from the same manufacturer but not the same batch. Hence, small differences may exist between the clinker of the OPC and the clinker used here. Furthermore, the sulfate carriers in the OPC were interground during its production. Consequently, differences between the commercial OPC and the ArCs prepared in this study will already originate from the way of fabrication even if the sulfate carrier amounts would be the same. For this reason, only ArC samples are presented in the following sections. The commercial OPC will be only discussed for comparison later.

3.2 | Pore solution analysis

To understand the impact of different sulfate carriers on cement hydration with added TEA, the elemental concentrations in the pore solutions extracted from pastes of the ArCs were determined (Figure 2). All samples without TEA show comparatively low [Si], [Fe], and [Al] (elemental symbols in brackets indicate concentrations). The ArCs with HH and MX show a higher [Ca] and [S] compared with the other samples, which is likely caused by the high dissolution rate of hemihydrate.

The increasing dosage of TEA leads to a gain in [Al] and [Fe] in the solutions for all the samples. This gain is especially strong for AH/2.88 and MX/2.88. An increase in [Al] and [Fe] with TEA has already been reported and is widely accepted to be caused by the complexation of aluminum and iron species with TEA. The same trend of the concentrations can be observed for [Si] and in most cases for [K] and [Na] as well. The increase in the latter two elements is also a likely reason for the increasing pH values that were detected especially for the pastes with AH and MX. Only for the paste with HH, a slight decrease in [K], [Na], and the pH value can be seen.

As the samples differ only in their sulfate carriers, the most considerable impact would be assumed to be found for [Ca] and [S]. Indeed, these two elements strongly depend on the used sulfate carrier. Additionally, the trends with a rising dosage of TEA are highly diverse, and both elements are strongly correlated with each other. However, the most crucial observation is that the ArC containing a mixture of sulfate carriers (MX/2.88, Table 2) and the commercial OPC (which also contains all three sulfate carriers, Table 1) show a substantially more prolonged induction period than the ArCs with only one sulfate carrier.

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For AH/2.88 and MX/2.88, a substantial decrease in [Ca] and [S] can be found with an increasing TEA dosage. These two ArCs are the ones in which the main hydration is most retarded (Figure 1).

In addition, a close correlation can be found for [Al], [Fe], [Si], [K], and [Na], but it seems to be also a connection to [Ca] and [S]. Samples that show a strong decrease in [Ca] and [S] with the addition of TEA have a vigorous increase in [Al], [Fe], [Si], [K], and [Na]. A slight increase in [Ca] and [S] is connected to a weak increase in [Al], [Fe], [Si], [K], and [Na]. In most cases, the highest concentrations of [Al], [Fe], [Si], [K], and [Na] are achieved by the samples MX/2.88 and AH/2.88 with 0.5 wt.% TEA.

Without TEA, the elemental concentrations in MX/2.88 are close to those in HH/2.88, while comparable elemental concentrations can be found for MX/2.88 and AH/2.88 at a TEA dosage of 0.5 wt.%. This indicates that the addition of TEA can alter which of the calcium sulfates has the strongest influence on the elemental composition of pore solution in a paste with several sulfate carriers.

**FIGURE 2** Elemental concentrations and pH values of pore solutions of artificial cements (ArCs) depending on the dosage of triethanolamine (TEA) after 5 min of undisturbed hydration and 10 min of centrifugation. The pH value was calculated based on the charge balance. The error bars indicate the standard deviation for the measured elemental concentrations [Color figure can be viewed at wileyonlinelibrary.com]

**FIGURE 3** Ratios of elemental concentrations in the pore solution of artificial cement (ArC) pastes dependent on the dosage of triethanolamine (TEA). The error bars indicate the standard deviation as calculated by the equation Equation S1 in the Supporting Information [Color figure can be viewed at wileyonlinelibrary.com]
The impact of TEA on [Ca] and [S] strongly depends on the sulfate carriers in each sample, but in every case, a similar trend for both elements can be observed with an increasing TEA dosage (Figure 2). Furthermore, there is a close dependence of [Al], [Fe], and [Si] on each other and on [Ca] and [S]. To investigate these apparent relations, the following ratios of elemental concentrations are plotted in Figure 3: [Ca]/[S], [Fe]/[Al], [Fe]/[Si], and [Al]/[Si]. A general increasing trend of [Fe]/[Al], [Fe]/[Si], and [Al]/[Si] due to the addition of TEA can be found for nearly all samples. The high values of [Fe]/[Al] and [Fe]/[Si] with 0.1 and 0.5 wt.% TEA indicate that TEA has stronger complexation capability for iron as the central element. In addition, the [Al]/[Si] ratio also increases with rising dosage of TEA but is lower than the ratio [Fe]/[Si], which indicates an appreciable but compared with iron less strong complexation capability of TEA for aluminum.

In contrast to the increasing trends of [Fe]/[Al], [Fe]/[Si], and [Al]/[Si] for all the samples, the [Ca]/[S] ratio is only slightly impacted by the increasing dosage of TEA. A little increase in [Ca]/[S] can be observed for ArC with HH, whereas ArC with GS shows no considerable impact with TEA addition. The paste A/2.88 decreases strongly in [Ca]/[S] at 0.1 wt.% TEA, but a massive increase can be observed with the TEA dosage of 0.5 wt.%. This effect will be discussed later. Only the sample with three mixed sulfate carriers (MX/2.88) shows a continuous decrease in [Ca]/[S] with an increasing TEA dosage. It indicates again that the sample with the mixed sulfate carriers behaves differently than the samples with only one type of sulfate carrier.

### 3.3 Effect of sulfate carrier amount on the cement hydration

As described in the introduction, TEA can enhance the dissolution of the aluminate-containing clinker phases as well as of the sulfate carriers. Furthermore, the pore solution data show a substantial impact of TEA on the concentrations and ratios of the corresponding elements. Thus, the question arises how TEA impacts the interaction of aluminate-containing clinker phases with sulfate carriers, which should be examined further by changing the amounts of the sulfate carriers. The heat development of ArCs with different amounts of mixed sulfate carriers (MX) without and with the addition of TEA is shown in Figure 4.

For the samples without the addition of TEA, the change in the amount of the sulfate carrier does not affect the length of the induction period, and a comparable acceleration period can be found. The first significant difference between the samples is the earlier occurrence of the deceleration period in MX/1.44, which is likely because of the low amount of the sulfate carrier in this sample. In MX/1.44, the so-called “sulfate depletion” (exhaustion of calcium sulfate) happens during the main hydration of C₃S, which can lead to suppression of the heat flow of C₃S as already observed by other authors. In the other three samples, the sulfate depletion occurs later due to the higher amounts of the sulfate carriers. Hence, a longer time is needed for them to step into the deceleration period.

With the addition of 0.5 wt.% TEA, the differences in the hydration behavior of the four samples are much more substantial. The paste with 1.44 wt.% SO₃ (MX/1.44) has an induction period that is several times longer than that without TEA, and it shows a lower main peak. When the calcium sulfate addition is increased to 2.88 wt.% SO₃, the induction period shortens, but the height of the main hydration peak is still lower compared with the samples without TEA. The

![Figure 4](wileyonlinelibrary.com)
further increase in the amount of mixed sulfate carrier reduces the induction period. Moreover, a minor exothermic event (approximately at 2.75 h) occurs during the induction period. The increase in the SO₃ amount from 4.32 to 5.76 wt.% only causes small changes besides the intensification of the exothermic event at 2.75 h. For both samples, the induction period is slightly longer compared with the samples without TEA, and the maximum of the main hydration peak is later and lower, which is assumed to be caused by direct retardation of the C₃S hydration by TEA instead of the indirect effect originating from the accelerated reaction of aluminate-containing clinker phases.¹³

As shown above, the increase in the amount of mixed sulfate carriers from 2.88 to 4.32 wt.% SO₃ can substantially reduce the delay of the main hydration caused by TEA (Figure 4). As the type of sulfate carrier is also shown to have an enormous influence (Figure 1), the question arises which type of sulfate carrier plays the central role in the compensation of the impact of TEA. Figure 5 shows a comparison of the heat development during the hydration of the samples MX/2.88, MX/4.32, and three other samples with an overall SO₃ amount of 4.32 wt.% but with different proportions of each sulfate carrier. In these last three samples, the overall SO₃ amount of 4.32 wt.% was achieved by adding GS, HH, or AH to MX/2.88 (Table 2).

As shown in Figure 5, increasing the amount of the sulfate carrier with respect to MX/2.88 by the addition of AH (MX_AH/4.32) leads to a substantially shorter induction period and a slightly increased height of the main hydration peak (Figures 4 and 5). When GS is used (MX_GS/4.32, Figure 5), the induction period is as short as that of MX/4.32, but the height of the main hydration peak is still lower. Only the sample with the addition of HH experiences a hydration process comparable with that of MX/4.32. These results indicate that the compensation of the negative impact of TEA on the main hydration by adding more mixed sulfate carriers in MX/4.32 compared with MX/2.88 is primarily due to the increased amount of HH. Furthermore, the effectiveness of the sulfate carriers in suppressing the impact of TEA on the main hydration can be given as the sequence of hemihydrate > gypsum > anhydrite, which matches well with the dissolution rates of these calcium sulfates.

### 3.4 In-situ XRD

As described above, MX/2.88 shows the most prolonged induction period of all ArCs with this amount of sulfate carrier and TEA addition. It was also shown that increasing the sulfate carrier amount can shorten the induction period. To clarify the underlying mechanisms, pastes of GS/2.88, HH/2.88, AH/2.88, and MX/2.88 with and without TEA as well as MX/4.32 with TEA were examined using in-situ XRD (Figure 6 and Figure S2).

The consumption of the main clinker phases, as well as the precipitation of portlandite, occurs comparably in all samples without TEA (GS/2.88, HH/2.88, AH/2.88, and MX/2.88 with 0.0 wt.% TEA), which is consistent with the results of calorimetry (Figure 1). Besides, C₃S (Figure 6A and Figure S2A) dissolves in mainly the same manner in all samples; C₃AF (Figure 6D and Figure S2D) does the same. In approximately the first 8 h, C₃A (Figure 6B and Figure S2B) also behave comparably in all samples, while the revival of the C₃A hydration seems to be considerably more intense for pastes of GS/2.88 and MX/2.88. Gypsum (Figure 6E and Figure S2E) and anhydrite (Figure 6C and Figure S2C) are the only two types of calcium sulfate that can be detected. Hemihydrate cannot be observed, as it has a high dissolution rate.
rate that leads to fast reprecipitation as secondary gypsum (it should be noted that the intensity values of primary and secondary gypsum can be compared only qualitatively due to likely differences in the crystallite shape). The intensity of ettringite (Figure 6F and Figure S2F) shows a dependence on the sulfate carrier used. The MX/2.88 paste initially forms slightly more ettringite than the other samples, while its later intensity is nearly equal to that in AH/2.88 at the end of the observation.

The addition of 0.5 wt.% TEA to the four pastes with 2.88 wt.% SO₃ changes the results considerably. An intensification of the initial dissolution of the monitored clinker phases and the sulfate carriers can be observed. In the case of the main clinker phases, this intensification is the least for HH/2.88, followed by MX/2.88. C₃S experiences a comparably early dissolution in both pastes. The initial dissolution of C₃A in the sample with HH is nearly equal to that of all samples without TEA, whereas it is more intense for the sample with the sulfate carrier mixture (MX). The initial diffraction intensities of C₃S, C₃A, and C⁴AF are comparable for the pastes with GS and AH and considerably lower compared with HH/2.88 and MX/2.88. In the paste MX/2.88, the intensity development of C⁴AF is mainly similar to GS/2.88 and AH/2.88, whereas the paste of HH/2.88 again behaves almost like the samples without TEA. Hemihydrate seems to suppress the enhancement of the initial dissolution by TEA (HH/2.88), which could also be the reason for the intermediate behavior of MX/2.88.

As already mentioned, the initial dissolution of the calcium sulfates is also enhanced. Compared with the equivalents without TEA, the samples of HH/2.88 and AH/2.88 show considerably decreased intensities of secondary gypsum and anhydrite, respectively. In GS/2.88 and MX/2.88, calcium sulfates can only be recognized in the very beginning (gypsum and anhydrite, respectively). The strong consumption of the sulfate carriers in MX/2.88 matches well with the extremely intense precipitation of ettringite at the initial stage (Figure 6F), which is not observed for the samples with 2.88 wt.% SO₃ from single sulfate carriers (Figure S2F). In the further hydration, the paste MX/2.88 undergoes a remarkably substantial delay of the main C₃S hydration and portlandite precipitation (Figure 6G,H), which is in accordance

**FIGURE 6** Effect of different sulfate carrier combinations and amounts on phase development in artificial cements (ArCs) with 0.0 or 0.5 wt.% triethanolamine (TEA). In all panels except (H), the measured intensities are smoothed by a moving average of 10 values. The data lines in (D) are only drawn until this reflex is superimposed by another of portlandite [Color figure can be viewed at wileyonlinelibrary.com]
with the calorimetric analysis (Figure 1). Interestingly, the dissolution of C₃A revives apparently at the same time as the C₃S hydration.

When the amount of the sulfate carrier is increased as in MX/4.32, calcium sulfates can be detected by XRD with the addition of 0.5 wt.% TEA as well. Gypsum can be recognized in the first measurements but is consumed fast. Anhydrite gives an initial intensity slightly lower than in the sample AH/2.88 with TEA. After approximately 8 h, the development of the anhydrite intensity (Figure 6C) starts to be very close to that in the paste AH/2.88 with TEA. Surprisingly, the development of C₃S, C₃A, and C₄AF in MX/4.32 resembles that of GS/2.88 and AH/2.88 with TEA. The revival of the C₃A hydration starts at approximately 20 h, which matches well with the slight bending in the calorimetric curve (Figure 4A). The substantial retardation of the main reaction of C₃S as found in MX/2.88 is not observed, which corresponds well to the results of calorimetry.

In accordance with the main hydration of C₃S, the occurrence of X-ray-detectable portlandite is slightly earlier in MX/4.32 as well as in HH/2.88 compared with MX/2.88, GS/2.88, and AH/2.88, which is especially well visible for the basal reflex (Figure 6H and Figure S2H). Seemingly, high additions of hemihydrate (as in the samples HH/2.88 and MX/4.32) enable the pastes with 0.5 wt.% TEA to conduct earlier portlandite nucleation or growth. Furthermore, the higher amount of sulfate carriers contained in MX/4.32 in comparison with the other four TEA-bearing pastes leads to a slightly enhanced intensity of the diffractions of portlandite. The initially formed amount of ettringite in MX/4.32 is comparable with MX/2.88. However, the ettringite quantity is nearly constant in MX/2.88 after the initial hydration, but a continuously increasing amount of ettringite can be found in MX/4.32, especially after the revival of the C₃A hydration, which thus leads to a considerably higher amount of ettringite in MX/4.32 than these in the pastes with 2.88 wt.% SO₃, which is likely due to the higher calcium sulfate content.

3.5 | Comparison to chemical calcium sulfates

Finally, it was evaluated if the substantially more prolonged induction period in the sample MX/2.88 is due to the different states of calcium sulfate or if the impurities in the used sulfate carriers are the decisive factor. For this purpose, samples (equivalent to GS/2.88, HH/2.88, AH/2.88, and MX/2.88 with 0.5 wt.% TEA) were prepared using calcium sulfates of chemical grade instead of the industrial sulfate carriers (Figure 7). There are some differences in the time of appearance and the shapes of the main peak in calorimetry comparing samples with equivalent type of calcium sulfate. Nevertheless, the relative order of appearance of the main peaks is the same for the samples with chemical calcium sulfates as for those with industrial sulfate carriers. Likewise, the substantially stronger extension of the induction period can be recorded for the sample with three chemical calcium sulfates. Consequently, the different states of the calcium sulfates can be considered as the key factor provoking the differences in the times of appearance of the silicate reaction.

4 | DISCUSSION

Without the addition of TEA, the ArCs with 2.88 wt.% SO₃ behave nearly the same (Figure 1). However, at a dosage of 0.5 wt.% TEA, an entirely unexpected phenomenon was ascertained by calorimetry as well as in situ XRD: An ArC with three sulfate carriers (MX/2.88) shows a substantially more prolonged induction period compared with the other three ArC pastes with the equivalent amounts of single sulfate carriers (GS/2.88, HH/2.88, and AH/2.88). Consequently, the discussion focuses on the samples with TEA. A schematic drawing of the suggested chain of causation discussed below is provided in Figure 8.

The following characteristics were found for the ArC with a mixture of three industrial sulfate carriers, which shows a more substantial delay of the main silicate reaction compared with samples with only one sulfate carrier (Figures 1 and 8A–C): (1) extensive initial precipitation of ettringite (Figure 6 and Figure S2); (2) extremely early exhaustion of calcium sulfates (Figure 6 and Figure S2); (3) very low [Ca] and [S], as well as enhanced [Al] in the early pore solution (Figure 2).

Likely, the very intense early ettringite formation in MX/2.88 with 0.5 wt.% TEA causes a significant consumption of ions from solution, leading to a decrease in the
saturation of the calcium sulfates and consequently to enhanced dissolution as well as early exhaustion of the calcium sulfates (Figure 6 and Figure S2). Hence, the concentrations of calcium and sulfate reach comparatively low values in the solution and a relatively high aluminum concentration is observed (Figure 2). It is well-known that the [Al] in the pore solution increases strongly and remains at a high level after the exhaustion of the calcium sulfates, which is due to a change in the phase equilibria. Such an enhanced [Al] is a likely reason for the delayed main silicate reaction. Aluminum species in aqueous solutions have been reported to slow down the dissolution of C₃S, which is activated by TEA) is not substantially suppressed, and aluminum species can therefore go into solution with a higher quantity. On the other hand, however, [S] is high enough to lead together with the high [Al] to a strong super-saturation of ettringite in the solution overcoming the nucleation barrier (Figure 8C).

The limiting factor for the quantity of ettringite formed in MX/2.88 seems to be the availability of sulfate. Several observations support this. While aluminate-containing clinker phases can be detected over the whole time of observation, calcium sulfates exhaust very early (Figure 6 and Figure S2). The diffraction intensity of ettringite in MX/2.88 with TEA increases only slightly after the extensive initial precipitation (during which the calcium sulfates also exhaust). Possibly, this slight increase in later time is mainly caused by the sulfate desorbing from surfaces, which is used for further ettringite precipitation from the solution with high [Al]. Furthermore, the diffraction intensity of ettringite is comparable with the later intensity of the sample HH/2.88 containing the calcium sulfate with the highest dissolution rate and solubility (hemihydrate), which would be assumed to be the best supplier of calcium and sulfate.

The reasons why the samples with the same amount of calcium sulfate from one sulfate carrier (AH/2.88, HH/2.88, and GS/2.88) show a less intense initial ettringite formation with 0.5 wt.% TEA compared with MX/2.88 seem to be specific for each sample. The sample AH/2.88 with 0.5 wt.% TEA contains a high [Al] in its pore solution at the early stage, which is more than double than for MX/2.88 (Figure 2). This high [Al] together with the low dissolution rate of anhydrite could be suitable for the precipitation of AFm instead of ettringite. TG (Figure S3) and SEM (Figure S4) of samples after 5 min of hydration support this interpretation. Only the sample AH/2.88 with 0.5 wt.% TEA shows a signal in the weight derivative (dTG) at approximately 130°C (Figure S3), characteristic for AFm. The examination with the scanning electron microscope (Figure S4) reveals only for AH/2.88 a large number of thin, uneven sheet-like precipitates, which are likely AFm. However, the samples GS/2.88, HH2.88, and MX/2.88 have dTG signals (Figure S3) mainly distinctive for ettringite (<100°C) and gypsum (120°C). In these samples, SEM (Figure S4) indicates ettringite as the dominant precipitate, which can be recognized as hexagonal prisms or needles. To further characterize these precipitates, line scans of SEM-EDS were performed (Figure S5). The SEM-EDS shows that both types of precipitates contain aluminum and sulfur, consistent with
the identification as AFm and ettringite. AFm phases can incorporate a large variety of anions, but the detection of sulfur makes it likely that the AFm in the current samples is either SO$_3$-AFm or a solid solution of SO$_3$-AFm and OH-AFm potentially incorporating some carbonate. The extensive formation of AFm in the early hydration of AH/2.88 could be the cause of the unusual behavior of the [Ca]/[S] ratio depending on the TEA dosage in this sample (Figure 3).

Nevertheless, in AH/2.88, the retardation of the main silicate reaction is considerably less strong compared with MX/2.88 (Figures 1 and 6). The precipitation of the initially dissolved aluminum species as AFm instead of ettringite is indeed initiated by an undersupply of sulfate due to the lacking dissolution of anhydrite. Conversely, this process leads to a lower consumption of calcium sulfate during the initial hydration, which results in a late exhaustion of the sulfate carrier (Figures 6 and 8B). This might be the reason for the weaker retardation of the main C$_3$S reaction. The [Al] is initially high (Figure 2) but can be decreased by the further dissolution of anhydrite and the precipitation of ettringite and/or AFm (Figures 6 and 8B). Such a strong, successive decrease in the initially high [Al] in an OPC system with TEA has already been reported.

In the sample of HH/2.88 with TEA, the dissolution of hemihydrate also provides a large number of sulfate ions. However, the dissolution of C$_3$A and C$_4$AF is hindered (Figure S2) potentially by the abundant sulfate ions occupying the surfaces of the aluminate-containing clinker phases. Hence, the high [S] in the pore solution of HH/2.88 is connected to a low [Al] (Figure 2). Furthermore, the high sulfate concentration leads to the formation of secondary gypsum (Figure S2), which dissolves gradually for a longer time and keeps the high [Al] in the aqueous phase low.

The sample GS/2.88 with TEA contains a relatively high amount of sulfate in the early pore solution (Figure 2), and the initially dissolved quantities of the aluminate-containing clinker phases are relatively low (Figure S2). The gypsum depletes already very early, which possibly explains the decrease in intensity of C$_3$A and C$_4$AF observed in XRD in the first hour. The further hydration of C$_3$A starts after approximately 7 h (Figure S2). This is conceivably the reason for the deformed shape of the main hydration peak in the acceleration stage (Figure 1). The shoulder starting at approximately 7 h could be due to the further hydration of C$_3$A, and the temporary suppression of the C$_3$S hydration by the aluminum species released in the solution.

As seen in the case of the sample MX/4.32, an increase in the sulfate carrier amount can effectively reduce the retardation by TEA (Figures 4-6). The results of XRD show that comparable quantities of ettringite were formed in MX/4.32 and MX/2.88 at the very beginning. Nevertheless, the two samples mainly differ in the following two aspects: (1) the ettringite amount in MX/4.32 is continuously increasing along with the hydration time; (2) a large amount of anhydrite can be detected in MX/4.32 at a later time as well. This indicates that enough sulfate can be provided in MX/4.32 (in contrast to MX/2.88), which can lead to a low [Al] in the pore solution by the formation of ettringite. The long persistence of solid calcium sulfate leads to a later revival of the C$_3$A hydration and a long governance of the equilibrium with low [Al] in the pore solution. Consequently, the retardation of the silicate reaction by aluminum species is resolved.

Furthermore, despite the same added SO$_3$ amount of 4.32 wt.% only MX_HH/4.32 shows a hydration process comparable with MX/4.32 with 0.5 wt.% TEA (Figure 5). MX_GS/4.32 and MX_AH/4.32 have a lower main hydration peak or a lower main peak together with a prolonged induction period, respectively. As the effectiveness of the sulfate carriers in suppressing the impact of TEA on the main hydration matches well with the dissolution rates of these sulfate carriers, it is reasonable to deduce that the difference mainly originates from the dissolution rate of sulfate carriers. The lower the dissolution rate of sulfate carriers, the faster the dissolution of aluminate-containing clinker phases and the higher the [Al] in the pore solution, which finally results in the more severe retardation of the main hydration.

As no difference in the heat flow of ArCs with different sulfate carriers can be found without the addition of TEA (Figure 1), the sensitivity of ArC hydration to different sulfate carriers is apparently caused by the addition of TEA, which can significantly accelerate the dissolution of aluminate-containing clinker phases (Figure 6B,D and Figure S2B,D). It indicates that the original sulfate balance in cement can be broken by TEA, and the effect of TEA on the sulfate balance is significantly dependent on the type and amount of sulfate carriers in the cement.

5 | CONCLUSIONS

This study emphasizes the possible impact of chemical admixtures on the balances of sulfate carriers, aluminate-containing clinker phases, and clinker silicates in a Portland cement. Under the influence of TEA, a Portland cement containing a mixture of gypsum, hemihydrate, and anhydrite can show substantially stronger retardation of the C$_3$S hydration than similar Portland cements containing only one of these three sulfate carriers with the same molar amount of calcium sulfate.

The addition of TEA enhances the initial dissolution of C$_3$A and C$_4$AF, which leads to more substantial consumption of the sulfate carriers and potentially to their earlier exhaustion. In the case of Portland cement containing slow-dissolving anhydrite (like natural anhydrite), the enhanced
hydration of C₃S can be of a lower intensity as well as con-
tinuous ettringite formation consumes excessively sulfate from
the solution leading to nearly instantaneous exhaustion of
the sulfate carriers. This causes a permanently higher alu-
minate concentration in the solution. A result, the main
hydration of C₃S can be of a lower intensity as well as con-
siderably more retarded. The TEA-driven enhanced initial
dissolution of aluminate-containing clinker phases can con-
sequently disturb the original balance of the sulfate carri-
ers and aluminate-containing clinker phases. Increasing the
amount of sulfate carrier can greatly alleviate the retarda-
tion of TEA on main C₃S hydration, and hemihydrate plays a
more critical role than anhydrite and gypsum due to its
higher dissolution rate.

A dependence of Portland cement hydration on the type
and amount of the sulfate carriers should be taken into con-
sideration for all systems with the addition of admixtures,
which can possibly cause an activation of the aluminate-
containing clinker phases.

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CONFLICT OF INTEREST
The authors declare that they have no conflicts of interest.

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section.

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