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Formulation design of chloride-free cement additive by response surface methodology

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Abstract. The influences of chloride-free components of the cement additive: triethanolamine, triisopropanolamine, sodium hyposulfite and calcium gluconate on the 1d, 3d and 28d compressive strength of cement were investigated by response surface methodology. It found the early strength activators, triethanolamine and sodium hyposulfite could enhance the 1d strength of cement effectively but they did not contribute to the 3d strength enhancement, and further their interaction was able to decrease the 28d strength of cement. Calcium gluconate was not that effective for the strength enhancement on 3 and 28 days when it's simply dosed. However the interaction effect of calcium gluconate with triisopropanolamine could strongly favor the strength enhancement of cement after 3 days. Results indicated it was necessary to focus attention on the potential interactions among the chemical components. And for the concern of four chemicals studied in this paper, it was feasible to formulated a kind of chloride-free cement additive that can be effective for the early strength of cement and its the strength after 3 days.

Keywords: cement additive; chloride-free; interaction; strength of cement; response surface methodology

1. Introduction

Cement additive, which is also called grinding aids, is a special construction chemical that is widely used in comminution process of cement manufacture. The application of cement additive can not only reduce the agglomeration in the ball mill, but also modify the particle distribution of finished cement (Heren and Ö lmez 1997, Tsakiridis *et al*. 2009). The primary components of cement additive are alkanolamines or alcohols, they are directly fed with clinker, SCMs and gypsum into mill and ground together. Alkanolamines such as triethanolamine (TEA) and triisopropanolamine (TIPA) are able to promote the dissolutions of C_3A and C_4AF phases, however their impacts on other phases in clinker are still disputed (Gartner and Myers 1993, Heren and Ö lmez 1997, Tsakiridis *et al*. 2009, Huang and Shen 2014). In addition, the use of cement additive is able to increase the SCMs content in finished cement. Thus it requires that the strength of reduced clinker must be improved by cement additives. Chlorides normally are the popular accelerator to cement since they boost the early hydration of clinker minerals, promoting 1d and

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3d strength significantly (Singh and Ojha 1981). As a matter of fact, chlorides can be found in the most formulation of cement additive which is effective to early strength promotion. Despite of this, the use of chlorides is still limited since the researches confirmed that chlorides brought potential corrosion to the steel fiber in reinforced concrete and consequently influenced the durability of concrete structure. Chinese national code strictly regulates the chloride content in cement should be less than 0.06% (GB175-2007 2007). Some other non-corrosive accelerators were also studied. These accelerators were sodium hyposulfite ($Na_2S_2O_3$), calcium nitrate ($Ca(NO_3)_2$), sodium thiocyanate (NaSCN), etc. (Wise *et al*. 1995, Taylor 1997, Ramachandran *et al*. 2002, Chikh *et al*. 2008) These compounds were proven to increase the early hydration rate of cement to contribute to the early strength gain of cements or concretes. Considering both of the solubility and the economy, sodium hyposulfite is the first choice that can be the substitute for chloride being formulated in current cement additives. In the titled study, the effects of chloride-free combinations on strength of cement were supposed to be determined. An efficient statistical approach was used to arrange the experimental runs and to analyze the results.

2. Experimental

2.1 Raw materials

The 42.5R cement was used and was analyzed by XRD, XRF and PSD. XRD data was collected on a X'ARL using Cu Kα radiation (λ=0.154 nm) running in reflection geometry (θ/2θ) at room temperature. The data was collected from 10° to 70° (2θ) during ~ 60 min with a step size of 0.02°. The X-ray tube worked at 40 kV and 40 mA. Chemical analysis of cement was carried out by melting method for XRF exam. And the cement powder was dispersed by ethanol and was tested by Malvern Mastersizer. The mineral and chemical compositions of cement are shown in Fig. 1 and Table 1, respectively. Information of PSD is shown in Fig. 2. Triethanolamine, triisopropanolamine, sodium hyposulfite and calcium gluconate ($Ca(C_6H_{11}O_7)_2$) were all in chemical grade. And their maximum dosages were determined by experience and they were 0.02%, 0.02%, 0.06% and 0.02%, respectively, by mass of cement. Each chemical was diluted to 1% aqueous solution and was added into mixing water for cement mortar preparation.

Table 1 Chemical analysis on the 42.5R cement

Chemical composition	wt.%
CaO	61.3
SiO_2	22.7
Al_2O_3	6.8
SO_3	4.3
MgO	1.26
K_2O	1.08
Na_2O	0.1
LoI	3.0

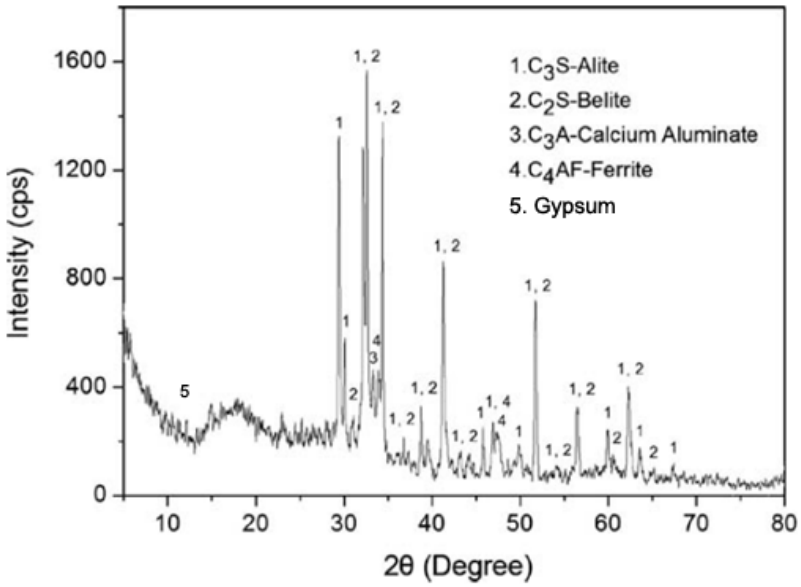


Fig. 1 XRD pattern of 42.5 R cement

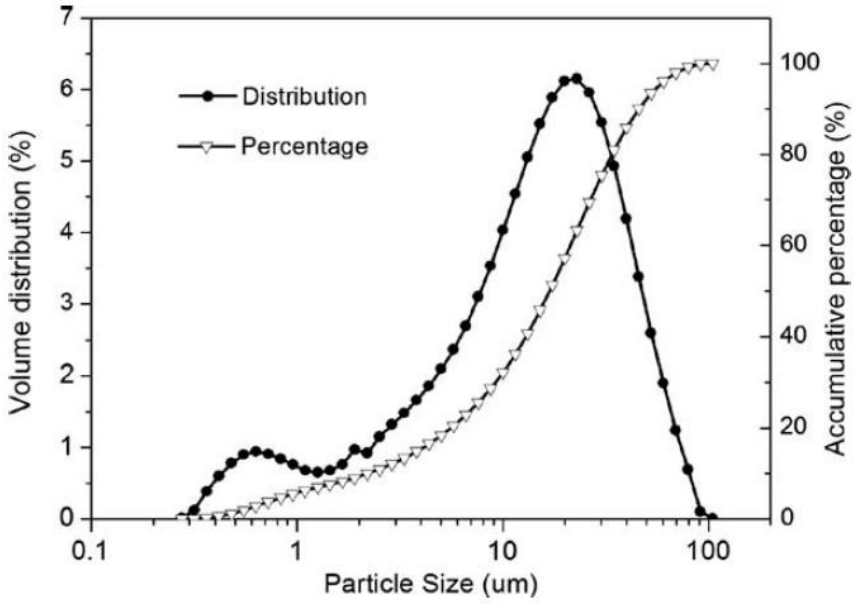


Fig. 2 Particle size distribution of 42.5R cement

2.2 Test method

The performances of these four chemicals were evaluated by the compressive strength of corresponding treated cement. Cement mortar was prepared according to GB/T17671. Each batch for three test specimens shall consist of (450±2) g of cement, (1350±5) g of ISO standard sand and

(225±1) g of mixing water. For avoiding the influence of moisture fluctuation from curing condition, the surface of cement mortar was covered by a piece of plastic membrane immediately after the mould was casted, and then the mould should be kept in moist air chamber with curing temperature of 20±1℃ and with 95±2% RH. The plastic membrane should not be removed during first 24 h initial curing. Demoulding should be done after initial curing to obtain the hardened specimens. Submerge the specimens vertically in water at 20±1℃ until compulsory ages for compressive strength test (3d and 28d). In addition, 1d's compressive strength of the specimens was also tested since it is an important criterion to evaluate the early performance of treated cement.

2.3 Statistical model

Response surface methodology (RSM) was applied to design the testing combinations of the chemicals to identify the significance of each chemical and so as to their interactions(Myers, Montgomery et al. 2009). RSM explores the relationships between multiple independent variables and one or more responses. The mechanism of RSM design can be visually described in Fig.3 where dots stand for the testing point in the middle of the edge while the star stands for the central point in the center of the cubic(Montgomery 2005). The edge points with coordinates (x, y, z＝－1 or 0 or 1) representing the low, median or high dosage of chemicals were selected to test in order to compare the effectiveness of each chemical. The central point with fixed coordinate (x, y, z＝0, 0, 0) representing the mean dosage of chemicals was selected and was tested repeatedly to estimate the degree of experimental error for the modeled responses and to establish the degree of significance for each chemical. The dosages of chemicals are shown in Table 2.

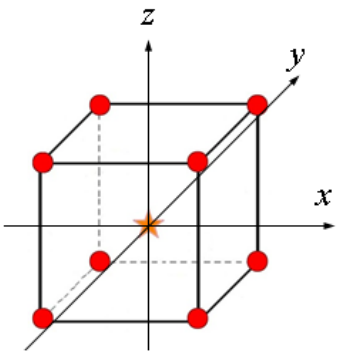


Fig. 3 Testing point of RSM

Table 2 Numbering and dosage information of each chemical

Component	Symbol	Low level		Intermediate Level		High Level	
		Code	Actual (wt%)	Code	Actual (wt%)	Code	Actual (wt%)
TEA	A	-1	0	0	0.01	1	0.02
TIPA	B		0		0.01		0.02
$Na_2S_2O_3$	C		0		0.03		0.06
$Ca(C_6H_{11}O_7)_2$	D		0		0.01		0.02

When fitting the model, analysis of variance (ANOVA) is used to judge the experimental error, the suitability of the model, and the statistical significance of the terms in the model (Montgomery 2005). Some terms may turn out not to be significant for a good representation of the experimental data, so usually a subset of model with fewer terms is selected. The p-value determines the appropriateness of rejecting the null hypothesis in a hypothesis test. It ranges from 0 to 1. The smaller the p-value, the smaller the probability that rejecting the null hypothesis is a mistake. As the alpha (a) level in this study was defined as 0.05, thus items in ANOVA with p-value greater than 0.05 are considered insignificant and should be omitted for the regression model. Lack-of-Fit (LoF) tests assess the fit of models. If the p-value is less than 0.05, evidence exists that the model does not accurately fit the data, thus the model needs to be revised. All the statistical design and analysis were done by Design Expert.

3. Results and discussions

3.1 Orders of importance of chemicals

RSM provided the least combination tests for four variables, they were triethanolamine (A: TEA), triisopropanolamine (B: TIPA), sodium hyposulfite (C: $Na_2S_2O_3$) and calcium gluconate (D: $Ca(C_6H_{11}O_7)_2$) investigated at low level (-1), intermediate level (0) and high level (1). The experimental matrix is presented in Table 3 in which a total of 30 trials were needed to run ANOVA. The experimental runs and the corresponding results are shown in Table 3 as well. The experimental data were analyzed by software and were further revised according to the above principles showing in Table 4.

Table 3 Design matrix of chemicals and compressive strength of corresponding cement

No.	Code combinations				Strength (MPa)			No.	Code combinations				Strength (MPa)		
					1d	3d	28d						1d	3d	28d
1	-1	1	1	1	20.0	40.7	62.1	16	-1	-1	1	-1	18.5	37.9	58.4
2	1	1	1	-1	20.3	38.2	57.3	17	1	-1	-1	1	18.7	37.9	56.2
3	0	0	-1	0	18.5	38.1	54.1	18	0	-1	0	0	19.1	38.6	55.2
4	1	-1	-1	-1	18.6	36.4	55.5	19	1	-1	1	1	20.4	36.1	55.2
5	0	1	0	0	21.0	37.3	57.8	20	0	0	0	0	18.6	37.5	53.7
6	-1	-1	-1	-1	17.5	36.4	56.2	21	-1	1	-1	-1	18.1	35.5	57.1
7	0	0	1	0	20.4	38.6	56.5	22	0	0	0	0	18.3	36.9	53.8
8	-1	-1	-1	1	17.0	35.6	58.0	23	0	0	0	-1	19.4	36.2	52.6
9	1	1	-1	-1	18.9	35.7	58.7	24	0	0	0	0	19.2	34.9	56.1
10	1	1	-1	1	20.7	40.2	61.6	25	0	0	0	0	20.9	37.2	54.6
11	1	1	1	1	20.6	39.5	61.1	26	-1	-1	1	1	17.8	36.8	58.6
12	1	0	0	0	19.5	35.9	56.1	27	0	0	0	1	20.1	38.2	54.4
13	-1	0	0	0	18.3	36.4	55.0	28	-1	1	1	-1	18.9	36.4	61.1
14	-1	1	-1	1	18.1	37.5	60.8	29	1	-1	1	-1	21.3	36.7	56.2
15	0	0	0	0	20.4	36.6	54.3	30	0	0	0	0	20.1	36.7	54.2

Table 4 Analysis of variance (ANOVA) of the RSM models for strength of cement

RSM items	p-value		
	1d	3d	28d
A	***0.0003***	0.4265	***0.0249***
B	***0.0290***	0.0571	< ***0.0001***
C	***0.0018***	0.0886	***0.0437***
D	0.5602	***0.0069***	***0.0014***
AB	0.3665	0.4413	0.1349
AC	0.6955	0.1212	***0.0118***
AD	0.6482	0.5718	0.9233
BC	0.4756	0.2500	0.7941
BD	0.1043	***0.0047***	***0.0165***
CD	0.6024	0.4132	0.1782
A^2	0.1195	0.0781	***0.0284***
B^2	0.4298	0.3116	***0.0009***
C^2	0.6428	0.1097	0.0670
D^2	0.8680	0.8619	0.2245
Lof	0.9586	0.4236	0.5011

It can be seen from Table 4, the p-values of LoF are great than 0.05, indicating the LoF is insignificant. Thus the RSM model fitted well with the statistical analysis of cement strength on all curing ages. In addition, the p-values of different RSM item less that 0.05 (marked in italic bold) suggested the corresponding chemicals or interactions significantly impacted the strength variation on different curing age. The summary of Table 4 can be summarized as following:

• For 1d strength variation of cement, the effects of TEA (A), TIPA (B) and $Na_2S_2O_3$ (C) were significant, and the importance order of symbol was A>C>B;

• For 3d strength variation of cement, the effects of $Ca(C_6H_{11}O_7)_2$ (D) and its interaction with TIPA (B) were significant, and the importance order of symbol was BD>D;

• For 28d strength variation of cement, all the chemicals and their interactions contributed to the strength variation, and the importance order of symbol was B>D>AC>BD>A>C. In addition, A^2 and B^2 indicated that the thresholds of corresponding chemicals existed.

3.2 Behavior of each chemical

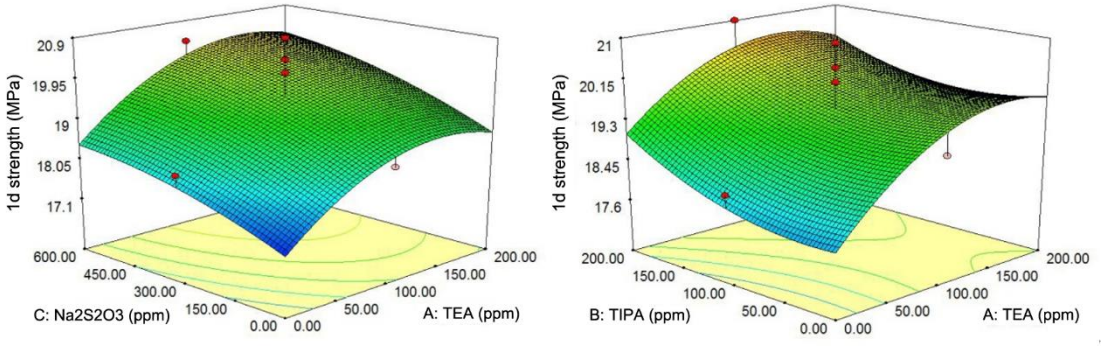
Table 4 showed the differences in p-values among different chemicals, and only the importance orders could be given. In order to interpret how each chemical impacted the strength variation on different curing ages, the 3-D surface plot was introduced to explain how chemicals as well as their potential interactions behaved. In a 3-D surface plot, a curved surface indicating the correlation of two variables is provided in a three-dimensional coordinate, with curves of equivalent values on curved surface projecting into X-Y plane.

As it suggested in Table 4, TEA, TIPA and $Na_2S_2O_3$ significantly impacted 1d strength of cement. In Fig. 4(a) it shown with the increased dosages of both TEA and $Na_2S_2O_3$, the 1d strength

of cement increased markedly. TIPA also contributed to the 1d strength, however its effectiveness was weaker than that of TEA since the increased rate of strength gain caused by TIPA was lower than that of TEA (Fig. 4(b)), which was in line with the importance order given in Table 4. In addition, provided by the surface plot, it shown that once the dosage of TEA exceeded 0.015% (150 ppm), its effect on strength enhancement weakened. And the increased additions of TIPA and $Na_2S_2O_3$ (0~0.02% and 0~0.06%, respectively) continuously favored the 1d strength gain.

As it suggested in Table 4, $Ca(C_6H_{11}O_7)_2$ and its interaction with TIPA contributed to 3d strength enhancement of cement. In Fig. 5, it shown that when TIPA was singly added, it barely given the strength gain. When $Ca(C_6H_{11}O_7)_2$ was added alone, it slightly enhanced 3d strength of cement. It's pronounced to see that when both TIPA and $Ca(C_6H_{11}O_7)_2$ added in high additions (0.02% or 200 ppm), their joint effect significantly contributed to 3d strength gain of cement. The surface plot further suggested that the strong interaction of these two chemicals only occurred in the condition in which TIPA>0.01% and $Ca(C_6H_{11}O_7)_2$>0.005%.

All the chemicals and their interactions influenced the 28d strength of cement significantly, which are displayed in Fig. 6. It suggested that TEA and $Na_2S_2O_3$, as well as TIPA and $Ca(C_6H_{11}O_7)_2$ strongly interacted, however these two interaction influenced the 28d strength of cement differently. In Fig. 6(a) it suggested that the interaction of TEA and $Na_2S_2O_3$ induced an adverse effect to cement strength. The combination of TEA at ≈0.01% (100 ppm) and $Na_2S_2O_3$



(a) TEA vs. $Na_2S_2O_3$ (b) TEA vs. TIPA

Fig. 4 Impacts of chemicals on 1d strength of cement

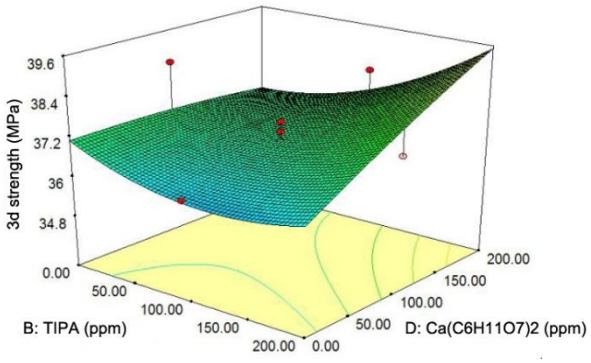
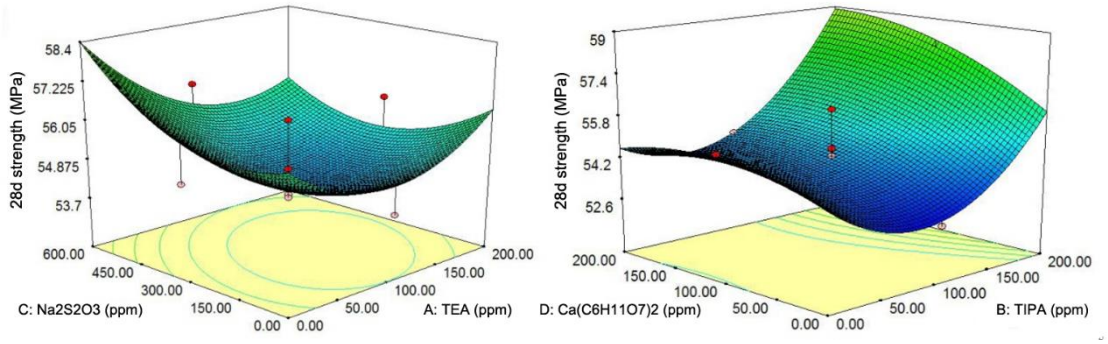


Fig. 5 Impacts of chemicals on 3d strength of cement (TIPA vs. $Ca(C_6H_{11}O_7)_2$)



(a) TEA vs. $Na_2S_2O_3$ (b) TIPA vs. $Ca(C_6H_{11}O_7)_2$

Fig. 6 Impacts of chemicals on 3d strength of cement

at 0.015~0.03% (150~300 ppm) reduced the 28d strength of cement markedly. TIPA interacted with $Ca(C_6H_{11}O_7)_2$ at high addition level as it's shown in Fig. 6(b). When TIPA was added alone, it's effective only within high addition level (>0.015% or 150 ppm). Compared with TIPA, the single addition of $Ca(C_6H_{11}O_7)_2$ slightly promoted the strength of cement on 28 days. However with the combination of TIPA, $Ca(C_6H_{11}O_7)_2$ strengthened the effect of TIPA. It could be read that the high interaction of TIPA and $Ca(C_6H_{11}O_7)_2$ took place at the additions of TIPA>0.015% (150 ppm) and $Ca(C_6H_{11}O_7)_2$>0.005% (50 ppm).

3.3 Discussions

The RSM analysis on cement strengths showed that the influences of TEA, TIPA, $Na_2S_2O_3$ and $Ca(C_6H_{11}O_7)_2$ on strength variations were different. The presences of TEA and $Na_2S_2O_3$ brought a positive effect on 1d strength of cement, however their strong interaction impacted 28d strength, which indicated that it's necessary to consider the influence of early strength promotor on strength development at late stage (Dodson 1990). And in terms of formulation design, such an adverse interaction should be avoided or be compensated. Gluconates, in various studies, are regarded as the typical retarder that prolongs the setting of cement (Singh 1976, Perez 2007). In our work, it showed that the addition of $Ca(C_6H_{11}O_7)_2$ with TIPA was able to enhance the strength of cement after 3 days, which suggested the combination of these two chemicals could be formulated to compensate the strength reduction resulted from the negative effects of early strength promoters. It is proposed that the retarder acted as a delayed accelerator due to its ability to be adsorbed onto the nuclei of hydrates and then poisons their growth, thus promoting the formation of more nuclei. Once the gluconate was consumed, a period of heterogeneous growth followed, producing higher surface areas due to the large number of nuclei. The addition of gluconate has also resulted in a higher diffusion coefficient, indicating that the C–S–H formed was more permeable, which further promoted the effect of TIPA. By such a statistical analysis, it can be concluded that by the correct combination of different chemicals, it's possible to formulate a chloride free cement additive that is able to guarantee the strength enhancement of cement on all curing ages.

4. Conclusions

A statistical approach was applied to identify the effect of each chemical on strength development of cement.

• TEA, $Na_2S_2O_3$ and their interaction strongly promoted the strength of cement on 1 day. Compared with them, TIPA was the less effective chemical to early strength enhancement;

• TEA and $Na_2S_2O_3$ were ineffective to 3 days strength enhancement, and the neither did the singly added TIPA. $Ca(C_6H_{11}O_7)_2$ interacted with TIPA contributing to the strength enhancement of cement, and their interaction took place at the additions of TIPA>0.01% and $Ca(C_6H_{11}O_7)_2$>0.005%;

• TEA, $Na_2S_2O_3$ and their interaction brought an adverse effect on strength enhancement of cement on 28 days, and such an interaction additions (TEA≈0.015%, $Na_2S_2O_3$ at 0.015~0.03%) should be avoided. The interaction of TIPA and $Ca(C_6H_{11}O_7)_2$ strongly favored the strength development of cement on 28 days, and their interaction occurred at additions of TIPA>0.015% and $Ca(C_6H_{11}O_7)_2$>0.005%.

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