

The Chemistry and Technology of **GYPSUM**

R. A. Kuntze, editor

ASTM **STP 861**

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THE CHEMISTRY AND TECHNOLOGY OF GYPSUM

A symposium sponsored by
ASTM Committee C-11 on
Gypsum and Related Building
Materials and Systems
Atlanta, GA, 14–15 April 1983

ASTM SPECIAL TECHNICAL PUBLICATION 861
Richard A. Kuntze, Ontario Research
Foundation, editor

ASTM Publication Code Number (PCN)
04-861000-07



1916 Race Street, Philadelphia, PA 19103

Library of Congress Cataloging in Publication Data

The Chemistry and technology of gypsum.

(ASTM special technical publication; 861)

“ASTM publication code number (PCN) 04-861000-07.”

Includes bibliographies and index.

1. Gypsum—Congresses. I. Kuntze, Richard A.

II. ASTM Committee C-11 on Gypsum and Related Building Materials and Systems. III. Series.

TA455.G9C48 1984

666'.92

84-70880

ISBN 0-8031-0219-4

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Library of Congress Catalog Card Number: 84-70880

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Printed in Ann Arbor, MI
September 1984

Foreword

The symposium on The Chemistry and Technology of Gypsum and Gypsum Products was presented at Atlanta, GA, 14–15 April 1983. The symposium was sponsored by ASTM Committee C-11 on Gypsum and Related Building Materials and Systems. Richard A. Kuntze, Ontario Research Foundation, presided as chairman of the symposium and is editor of the publication.

Related ASTM Publications

Masonry: Materials, Properties, and Performance, STP 778 (1982), 04-778000-07

Extending Aggregate Resources, STP 774 (1982), 04-774000-08

Cement Standards—Evolution and Trends, STP 663 (1979), 04-663000-07

Significance of Tests and Properties of Concrete and Concrete-Making Materials, STP 169B (1978), 04-169020-07

A Note of Appreciation to Reviewers

The quality of the papers that appear in this publication reflects not only the obvious efforts of the authors but also the unheralded, though essential, work of the reviewers. On behalf of ASTM we acknowledge with appreciation their dedication to high professional standards and their sacrifice of time and effort.

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Retardation of Gypsum Plasters with Citric Acid: Mechanism and Properties

REFERENCE: Koslowski, T. and Ludwig, U., “Retardation of Gypsum Plasters with Citric Acid: Mechanism and Properties,” *The Chemistry and Technology of Gypsum*, ASTM STP 861, R. A. Kuntze, Ed., American Society for Testing and Materials, 1984, pp. 97–104.

ABSTRACT: The object of the investigation was the retardation of gypsum plasters with citric acid. For that purpose measurements were carried out to get information about the mechanism of set retardation and the influence of citric acid on the microstructure and properties of gypsum plasters. Citric acid acts as a retarder by forming citrate. The citrate affects the nucleation and the crystal growth of gypsum by adsorption. That entails the retardation of the hydration period and the habit modification. The influence on the microstructure was investigated by means of the quantitative image analyses and by X-ray methods. Citric acid changes the properties of fresh and hardened mortars. The volume of setting and hardening gypsum plaster passes through a minimum. Increasing citric acid additions raise the minimum and decrease the following expansion. Strength formation was measured by binding and compressive strength tests and by Brinell hardness determination. With increasing citric acid addition, paralleled by higher humidities, a strong decrease in strength can be observed. In addition, the influence of citric acid on the creep behavior of hardened gypsum was examined.

KEY WORDS: citric acid, gypsum, mechanical properties, mechanism of set retardation, microstructure of retarded gypsum mortars, texture index, strength, creep properties

It is of the greatest importance for a given application to adjust a controlled setting and hardening of gypsum mortars. For this purpose retarding and accelerating agents are used in practice.

The one layer wall finish, for instance, requires a retardation of the gypsum plaster.

The object of this research work is the investigation of the mechanism of retardation of gypsum plaster by the addition of citric acid and its influence on the properties of the fresh and hardened mortar. The significance of this work lies in the explanation of the retardation mechanism and its close connection with the microstructure and hence with the mortar properties.

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Starting Materials

The main physical and technological research work was done with an industrial plaster of paris. Synthetic hemihydrate prepared from dihydrate (MERCK 2161) and autoclaved α -hemihydrate were used for the examination of the retardation mechanism.

Experimental Procedure

The retardation mechanism was investigated by

- (1) carrying out precipitation reactions as a function of the saturation,
- (2) measuring the calcium and sulfate concentrations of setting plasters,
- (3) measuring the adsorption of radioactive citric acid on the surfaces of hemihydrate and dihydrate as a function of time, and
- (4) examining the influence of the citrate formation on the retardation.

The microstructure of the hardened paste was investigated as a function of the citric acid addition by

- (1) analyzing the grain size distribution with the Endter-counter[®],
- (2) carrying out quantitative image analysis of pictures from scanning electron microscopy (grain size, circumference, area, and shape factor),
- (3) determining the texture index by means of X-ray, and
- (4) the determination of the porosity of thin sections (spherical shaped pores) and by means of a mercury pressure porosimeter.

The physical and technological properties were examined as a function of the citric acid addition by the

- (1) setting, the workability, and the strength according to German standard Gypsum Building Plasters; Terminology, Types and Application, Delivery and Marking, Requirements, Testing, Control (DIN 1168)
- (2) volume changes during setting as described by Ref 1,
- (3) creep of hardened gypsum plasters as a function of the humidity, and
- (4) moisture take up and the moisture expansion as a function of relative humidity.

More details of the experimental procedure are described elsewhere [2].

Results

Mechanism of Retardation

Citric acid acts as a retarder on hydrating gypsum plasters only together with other cations, mainly calcium ions and by forming citrate. But the needed cations

must be extracted from foreign compounds (for example, calcium carbonate and calcium hydroxide) and not from the calcium sulfates. Normal industrial plasters contain such compounds as impurities. In the case of very pure plasters a corresponding addition must be made. Besides gypsum plasters with a higher degree of acidity in comparison to citric acid must be neutralized first.

If the citrate formation is realized the retardation will run in two steps as shown in Fig. 1.

1. Directly after mixing, the citrate will be adsorbed onto the surface of the hemihydrate and hinder nuclei formation.
2. With an increased content of the citrate an adsorption will take place on the dihydrate nuclei and on the surface of the growing gypsum crystals.

The reduction of the nuclei formation (Step I) leads to fewer but larger dihydrate crystals. Increasing absorption on the surface of the dihydrate crystals (Step II) changes the morphology from needle-like to compact-shaped crystals.

Citric acid and calcium hydroxide cause a higher rate of citrate formation than calcium carbonate does. Bigger grain sizes and higher crystallization, especially of the carbonate, lower the formation rate additionally. These differences in the formation velocity lead to a more Step I type retardation with calcium hydroxide

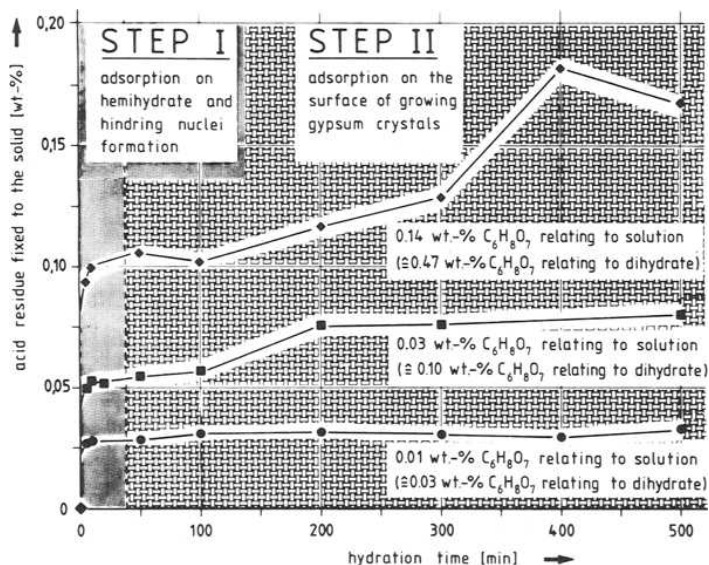


FIG. 1—Stepwise fixation of citrates on the dehydrated calcium sulfate (Step I) and the nuclei or on the growing dihydrate crystals, respectively (Step II).

and a partly more Step II type retardation with calcium carbonate as a Ca-ion donator.

The increase in the specific surface of the dehydrated calcium sulfates requires a higher amount of retarder addition. This fact is of greater interest with respect to the aging plasters.

In the present research work the addition of citric acid did not cause any change in the solubility of the hemihydrate. But with an equal water/gypsum ratio a decrease of the viscosity was observed with increased citric acid addition.

Influences on the Microstructure of Hardened Mortars

The retardation of the hydration of setting gypsum plasters greatly effects the microstructure of the hardened gypsum. In detail, increased citric additions caused the following alterations.

- (1) a linear increase of the average grain size together with a decrease of the quantity of grains per volume unit,
- (2) a broader grain size distribution,

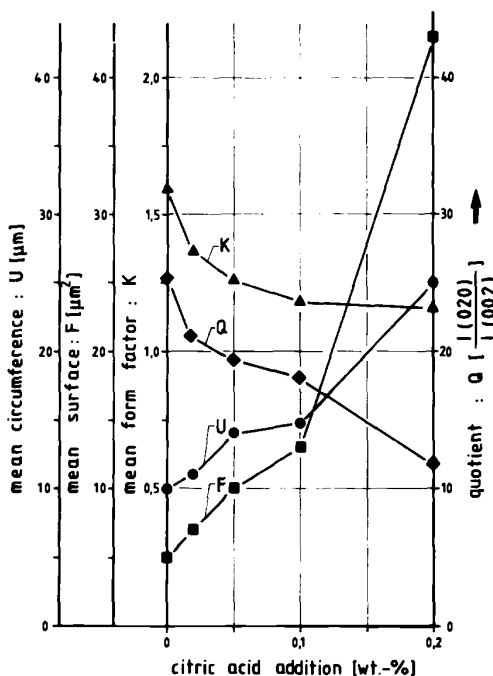


FIG. 2—Grain structure parameter as a function of citric acid admixture (addition in weight % of hemihydrate).

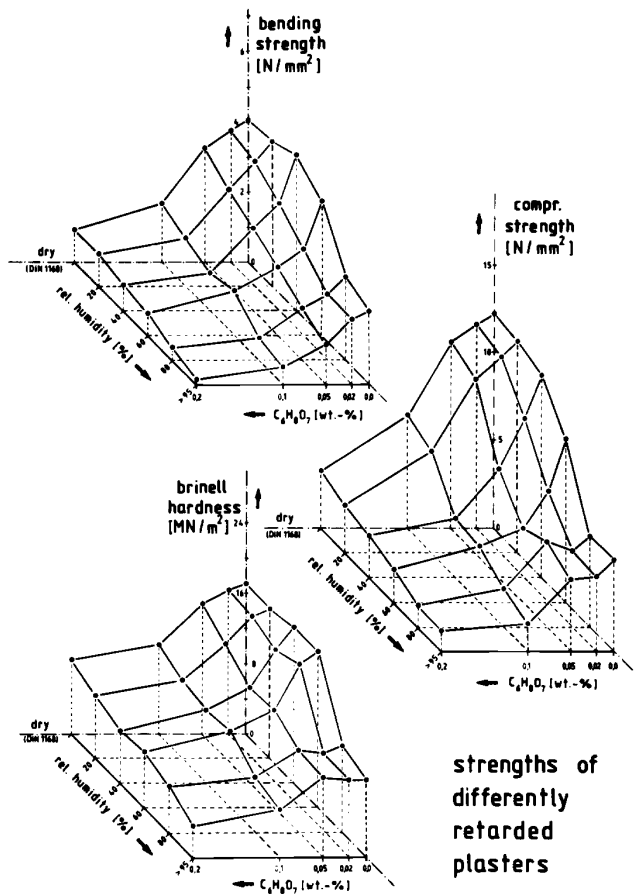


FIG. 3—Strength formation as a function of citric acid admixture and relative humidity of hardened gypsum mortar.

- (3) a hyperbolic change of the grain shape from long prismatic to compact prismatic,
- (4) an increased uniformity of the grain shape, and
- (5) a development from sphaerolitic crystal growth to isolated crystals.

The alterations can be partly derived from Fig. 2. The figure shows the measured increase of the average circumferences U and areas F , and the decrease of the shape factor K and of the texture index Q above increased citric acid additions. More details of the experimental data are given elsewhere [2].

A further alteration of the microstructure is caused by the rate of citrate

formation. A slow rate causes a more distinct change of the crystal shape towards a compact one while a higher rate causes smaller changes of the grain size and of the shape factor.

Finally, the analysis of the microstructure by means of the quantitative image analyzer gives more distinct and many sided information than by X-ray. On the other hand it takes less time to get results with the latter method.

Citric acid addition not only causes changes in the solids but also in the porosity, namely

- (1) a decrease of the open (total) porosity,
- (2) an increase of the average pore diameters, and
- (3) an increase of the diameters of air bubbles with a corresponding decrease of the amount of smaller bubbles.

These effects are in good agreement with the changes of the solid structure. Moreover they depend on the lower viscosity and on the setting retardation of the fresh mortar.

Influences on the Properties of Fresh and Hardened Mortars

Increasing citric acid additions result in increasing setting retardation. Besides the setting interval—the time between initial and final set—becomes broader.

The short-time workability of mortars with added citric acid is increased already by small admixtures of 0.02% (w/w). Higher amounts did not result in a further increase but may lead to a stabilization of the workability for a longer period.

The volume of setting and hardening gypsum plaster passes through a minimum. This occurs because of an early chemical shrinkage at a lower viscosity of the mortar and because of the crystallization pressure after reaching a certain viscosity, which may be at the end of the setting. Increasing citric acid additions will increase the minimum and decrease the following expansion. The additional influence of an increased water/gypsum ratio results in an increased relative expansion for the retarded pastes and a decreased expansion for the plain pastes.

The examination of the equilibrium humidity of hardened gypsum mortar versus a citric acid addition with the relative humidity as a parameter shows maximum water absorption at 0.025% (w/w) addition of citric acid. The absorption intensity decreases with the relative humidities.

Strength formation was measured by binding and compressive strength tests and by Brinell hardness determination on prisms with constant water/gypsum ratios. The retardation was done in this case with citric acid and calcite as a calcium-donor. The tests are carried out as a function of citric acid addition and of the relative humidity. Figure 3 shows a strong decrease in strength with increasing citric acid addition and higher humidities. With constant workabilities the drop in strength is significantly reduced. For low citric acid additions with

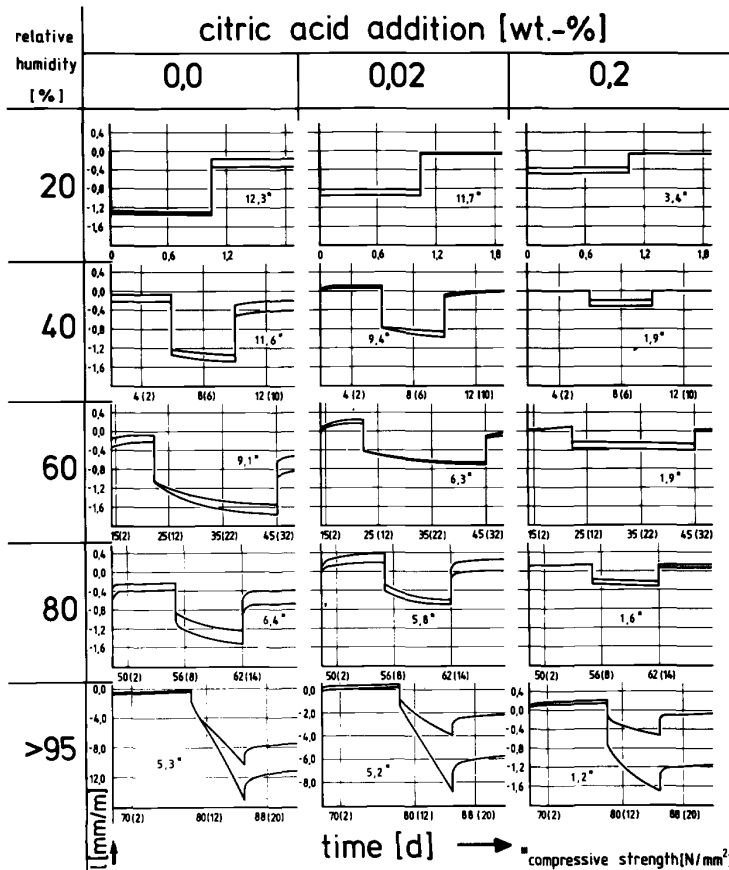


FIG. 4—Deformation time diagram loaded 20% of the compressive strength at the given humidity (first number: total time of the creep measurement; and in parenthesis: time of a single test cycle).

lower retardation rates no reduction in strength should occur. On the other hand citrate formed together with calcium hydroxide should also produce better strength.

Additional hardened gypsum was examined with regard to its creep behavior. Figure 4 shows the deformation time diagram of hemihydrate as a function of the citric acid addition and of the equilibrium humidity.

Without load the dihydrate shows an increased expansion with increased humidity. Maximum expansions are in the range of 1 mm/m. Unretarded and less retarded gypsum produced higher rates of expansion than highly retarded gypsum.

At 20% relative humidity the load dependent deformation is only an elastic one, which means the deformation is fully reversible in the deloaded state.

Increasing humidities, especially $>80\%$, result in increasing plastic, that is, irreversible deformation.

Increased retardation produces increased amounts of elastic deformation.

Summary

Calcium-citrate formation and its absorption on the surface of the hemihydrate, on the nuclei and on the growing dihydrate crystals, is the cause of retardation. An increasing citric acid addition leads to an increased grain size and to changes of the shape factor towards one. This change in grain size and in the shape factor results, along with an elongated setting time in

- (1) a higher plasticity of the fresh mortar,
- (2) less volume expansion during setting,
- (3) lower strength,
- (4) lower rates of humidity absorption,
- (5) lower rates of expansion caused by moisture adsorption, and
- (6) lower rates of plastic creep deformation favoring the elastic creep.

But these changes in properties again can be altered by changing the amount and the rate of citrate formation.

Acknowledgment

We thank the Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg, for the financial support of our experimental works.

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