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(54) Title: CONVERSION OF FLUOROANHYDRITE TO PLASTER

(57) Abstract

Gypsum plaster and gypsum wallboard products can be made from fluoroanhydrite by contacting the fluoroanhydrite with a reactive silica selected from the group consisting essentially of Portland cement; perlite; calcium, sodium or potassium silicates; pyrogenic colloidal silica and diatomaceous earth; and after gradual conversion of the fluoroanhydrite to substantially pure fluorogypsum, the purified gypsum is processed in customary fashion in the industrial manufacturing of plaster products. The reactive silica may be added to the fluoroanhydrite during the gradual aging conversion in water to fluorogypsum; or it may be added during water calcination of the fluorogypsum to stucco; or to the gauging water during gypsum plaster or wallboard product formation from the fluorostucco.

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Conversion of Fluoroanhydrite to Plaster

Background of the Invention

Field of the Invention

This invention relates to a process for transforming fluoroanhydrite into gypsum plaster and gypsum wallboard products.

Fluororanhydrite is a by-product in the manufacture of hydrogen fluoride from the sulfuric acid treatment of fluorite (calcium fluoride). Historically, the fluoroanhydrite, which is contaminated with sulfuric acid, is neutralized with lime or calcium carbonate additions and allowed to hydrate naturally over a several year period of time while weathering in waste heaps. It had been hoped that upon weathering such materials would then be usable in the industrial manufacture of various products. This has not proven to be the case.

Description of the Prior Art

Some early attempts to utilize the naturally weathered materials looked at the relationship of this material to Keenes cement (U.S. 1,304,148) and attempted to convert the weathering anhydrite material directly to the dihydrate form by the inclusion of various hydration catalysts and accelerators. Such proposed means to convert this waste product into an industrially usable product have focused upon the quick setting or hardening of the anhydrite content into a dihydrate material in the presence of reactive silica compounds coupled with pozzolonic materials and lime. See for example U.S. Patent Nos. 2,060,127; 2,606,128; 2,608,491 and the like. There is little demand for such inorganic binders; the primary commercial usage for calcium sulfate materials being in the formation of gypsum wallboard.

In addition to residual acids, fluoroanhydrite contains other impurities. Fluoroanhydrite or fluorogypsum can contain up to 2-3% fluoride, probably derived from unreacted calcium fluoride, together with smaller quantities of unreacted soluble and insoluble silicofluorides. These fluorine impurity species, probably a fluoroaluminum complex anion such as $[AlF_5H_2O^{-2}]$, impede the practical commercial conversion of the stockpiled material into calcium sulfate hemihydrate. First, these impurities inhibit the hydration of the fluoroanhydrite to gypsum. Secondly, they raise the calcining temperature for conversion of the fluorogypsum to stucco. Thirdly, they inhibit the setting of the stucco to a degree unreasonable for present day commercial wallboard formation and result in producing gypsum products of poor quality. Some of the residual fluoride species in the weathering stockpile material form compounds which are water soluble and may be washed away; while other species form water insoluble compounds that tend to co-crystallize with the dihydrate crystals being formed on weathering. These latter impurities, on attempts to convert the fluorogypsum to hemihydrate, cause extreme difficulties in the calcination conversion to hemihydrate and inhibit response of the formed stucco to set control agents. Further the stucco exhibits slow disintegration when mixed with gauging water. These are significant problems because all gypsum board lines employ set control agents as being critical in production rate and cost of production. Finally, stucco from such material exhibits low maximum rate of hydration and slow disintegration upon mixing with gauging water. This is critical in determining the strength of the set product. Natural gypsum, immediately after being calcined, characteristically disintegrates to a large degree upon dispersion in water. This disintegration may be measured as a large increase in the particle surface area. When fluoroanhydrite is neutralized with lime and hydrated, the resulting fluorogypsum it has been found, after being calcined to a fluorostucco, disintegrates only to a small degree upon dispersion, and the degree of disintegration is further reduced upon exposure to humidity such that an aged fluorostucco approaches the unpredictable, erratic dispersion properties of aged natural stucco unsuitable for building plaster or gypsum wallboard usage.

Summary of the Invention

It has now been found that by allowing a controlled gradual weathering of stockpiled waste fluoroanhydrite materials and calcination to calcium sulfate hemihydrate in the presence of a reactive silica, a truly industrially usable stucco is obtained. The impurities in fluorogypsum are present on the surfaces as well as throughout the crystal. Acid or water washing, particularly with grinding in between washings, is effective to remove the surface exposed impurities. Coupling this with calcination and hydration additives to remove co-crystalline impurities gives a combined effect making the material usable. The obtained fluorostucco has satisfactory calcination characteristics, rheological and physical properties customary to plaster made from natural gypsum rock when mixed with water and is suitable for formation into gypsum wallboard.

A part of the findings of the present invention is that while some of the fluorine and aluminum species contamination in by-product fluoroanhydrite can be removed by careful washing during the various conversion stages, complex species are trapped in the growing calcium sulfate crystal. By including reactive silicates during various stages of the processing, the crystallized species can either be inhibited in their growth and/or removed from the calcium sulfate crystals. Employing about 1-10% by weight of an active siliceous material in some manner frees the calcium sulfate from the poisonous fluoro and aluminum complex impurities that inhibit hydration of the fluoroanhydrite to gypsum, that inhibit subsequent calcination of the fluorogypsum to fluorostucco, that inhibit the setting action and strength development of the fluorostucco product.

Description of the Preferred Embodiments

The starting material is a residue from the process of manufacturing hydrofluoric acid from fluorospar. Fluoroanhydrite fresh from the reactor may be treated by the process of this invention and then stored for gradual conversion. Alternatively, or in addition, weathered stockpile material containing fluorogypsum as well as fluoroanhydrite may be treated. Alternatively, or in addition, treatment may be carried out during calcination of the fluorogypsum to fluorostucco. Thus, in one preferred embodiment, hot fluoroanhydrite directly from the reactor may be blended with the reactive siliceous material and passed to briquetting or pelletizing apparatus for mixing with a suitable binder while being formed into briquettes or pellets. The briquettes may then be warehoused or stockpiled while the conversion to fluorogypsum occurs. Thereafter, the fluorogypsum is calcined to fluorostucco for use as plaster products or subsequent rehydration in gypsum board manufacture.

Suitable active siliceous materials preferably include Portland cement, finely ground expanded perlite, diatomaceous earth, reactive colloidal silica such as Cab-O-Sil® silica or Aerosil® fumed pyrogenic silica and alkaline earth metal silicates such as sodium, potassium and calcium silicate. These are all siliceous products having high surface areas (greater than about 10,000 square centimeters per gram) and having chemically reactive sites due to surface deformaties, such as chemically incomplete silicon dioxide surfaces, missing oxygen atoms in the alkali metal silicates and Portland cement, or stressed crystal configurations in expanded perlite sintered or fumed silicas and diatomaceous earth. Other reactive siliceous products suitable for use in this invention will be evident from this description. Generally inclusion of about 1-10% by weight of the active siliceous material based on the weight of calcium sulfate present in the fluoroanhydrite will produce satisfactory results. Preferred amounts of siliceous material are dependent upon the time at which the material is added in the process and the particular siliceous material.

Extensive studies on a partially hydrated fluoroanhydrite-fluorogypsum stockpile material showed the material to be non-homogeneous, and calcination to stucco resulted in very slow setting even when accelerators were used. The slow setting properties were caused by poor disintegration of the stucco upon dispersion in water, and by a chemical interference to the growth of calcium sulfate crystals in the gypsum phase. In comparison to natural gypsum, calcination of the stockpile materials exhibited higher drag and dump temperatures. The resultant fluorostucco upon mixing with water had a smaller particle size initially, but a larger particle size upon dispersion. While having a surface area initially comparable to natural gypsum, the fluorostucco exhibited a lower surface area upon dispersion with water in a board machine mixer.

It is now believed that while some of the contaminant species are water and/or acid soluble and may be washed off the surfaces of the fluoroanhydrite or fluorogypsum, the difficult contaminant species are co-crystalline or occluded, i.e., as the fluoroanhydrite is undergoing the transformation to fluorogypsum, contaminant ions in the surrounding solution crystallize on the growing gypsum phase and are occluded or co-crystallized in the gypsum matrix. It has now been found that these contaminating ions can be rendered inactive in the solution phase, and then the gypsum which re-crystallizes is relatively free of impurities and has properties similar to those of natural gypsum.

The preferred first step for fresh or weathered fluoroanhydrite material is a water or dilute acid wash. For example, it has been found that washing the weathered material twice with water, with a light grinding in between washings, drammatically increased the surface area from about 6,000 cm^2/g to 15,900 cm^2/g; and reduces the set time with a standard amount of accelerator from approximately 12 minutes without washing to 6.3 minutes after the double washing. Apparently, the light grinding and second wash released some of the impurities. The same treatment steps using 32% sulfuric acid instead of water gave an even better accelerated set time response of 4 minutes. However, neither of these treatments provided sufficient strength or the dispersion disintegration characteristics of natural gypsum. Further, during calcination these materials were difficult to stir, had a high drag temperature and the calcination temperature was difficult to maintain and not uniform throughout the kettle.

Coupling this step with active siliceous material addition to inhibit co-crystalline impurities gives a combined effect making the fluoroanhydrite material usable for building plaster and gypsum wallboard production.

As one alternative, active siliceous materials may be added to the mixing (gauging) water of fluorostucco. For example, the following were evaluated as slurry additives to fluorostucco obtained by calcining different weathered fluorogypsum samples without any adjustments. The samples were from different locations in the fluorogypsum pile and analysis indicated widely varying degrees of hydration and chemicals content:

Slurry Addition Alone

Untreated Fluorostucco	Slurry Additive	Amount	Vicat Set Time[1]	Temperature Rise Set Time
Control	--	--	10.5 minutes	17.0
	Na_2SiO_3	1 gram	8.8	14.0

[1] Elapsed time from mixing 50 g. plaster with gauging water to when a 300 g. Vicat needle will not penetrate more than half way (20 ± 2mm) into the setting slurry.

From the results it is clear this addition rendered the co-crystalline impurity, non-interfering in the through solution setting of stucco recrystallizing as dihydrate.

As another alternative, active siliceous materials may be added to the fluorogypsum at the stage of calcination to fluorostucco. The additives were mixed with weathered fluorogypsum and then kettle calcined under standard conditions. Since kettle calcination itself is a topatactic dehydration, the additives at this point should have a surface effect rather than a crystallographic effect.

Calcination Addition

Additive	Amt. Added	Amt. Cal.	Drag Temp°F	Dump Temp°F	Hydration Analysis% Hem.	Dihyd.	Anh.	Other
Untreated - Control		4 kg	268	293	83.6	3.7	2.8	9.9
Na_2SiO_3	40g	4.04kg	273	302	86	2.1	1.7	10.2
Diatomaceous earth	80g	4.08kg	262	293	79	3.2	2.8	15
Portland cement	80g	4.08kg	266	293	81.5	2.8	2.9	12.8

From the table it may be seen that the additives did not significantly affect the calcination properties. Diatomaceous earth reduced the drag temperature by a slight amount, but still significantly above that of natural gypsum. Following calcination, the materials were evaluated for setting and disintegration properties of the fluorogypsum calcined with the additives:

Setting & Disintegration Properties of Calcination Addition

Additive	Accelerator	Vicat	Temp/Rise Set
Control Untreated	10 lb/ton	17.0 min	23.5 (w/o accel.)
		11.5	18.5 (w/acceler.)
Na_2SiO_3	10 lb/ton	13.8	18.5
		10.8	15.0
Diatomaceous earth	10 lb/ton	19.0	25.0
		12.0	19.0
Portland cement	10 lb/ton	16.2	23.0
		10.3	18.0

The subsequent rehydration of stucco when mixed with gauging water is a through solution process thus the additives having only a surface effect during calcination when carried through the rehydration also have a crystallographic effect. From the table it may be seen that sodium silicate and Portland cement shortened the with accelerator setting times and were thus found to increase accelerator response of the calcined fluorogypsum. Thus, it seems that the silicate active ion appears to have a beneficial effect. The diatomaceous earth increased the disintegration of the treated stucco to a level equal to that of natural land plaster; however, the set time was not affected.

Thus, while some of the contaminant species are water and/or acid soluble and may be washed off the surfaces of the fluoroanhydrite or fluorogypsum, the difficult-to-remove contaminant species are co-crystalline. As the fluoroanhydrite is undergoing the transformation to fluorogypsum, contaminant ions in the surrounding solution crystallize on the growing gypsum phase and are occluded in the gypsum matrix. The high drag temperature of the fluorogypsum demonstrates the adverse effect of even low concentrations of the impurities in the gypsum lattice. The impurity species, probably a fluoroaluminum ion complex such as $[AlF_5(H_2O)]^{-2}$, desensitizes the calcined fluorostucco to the presence of accelerators in the mixing water.

Fluoroanhydrate Hydration Additive

The additives listed below were mixed with fluoroanhydrite and neutralized gypsum pond water and allowed to weather hydrate over time. When the samples had hydrated to an appreciable extent above 70% gypsum they were kettle calcined without further additive addition to fluorostucco and the Vicat and temperature rise set times of the materials with and without 10 pounds per ton setting accelerator and gauging water without further additive addition were determined:

	Untreated	$CaSiO_3$ 1%	$CaSiO_3$ 2%	Perlite 1%	Perlite 2%	Portland Cement 1%
Hydration Rate	23% gypsum at 6 weeks	41% at 4 wks	59%* at 6 wks	75% at 4 wks.	78%	67% at 6 wks.
Calcination data						
Dry Temp. °F	266°F	268	268	255	257	255
% Hemihydrate	55.9%	72.4	72.42	70.66	61.79	60.39
% Dihydrate	-0-	-0-	-0-	0.82	-0-	2.20
% Anhydrite	4.75	3.05	3.05	2.56	11.24	14.76
% Other	39.35	24.53	24.53	25.96	26.97	22.63
Rehydration data						
Vicat Set (Minutes)						
w/o accelerator	4.3	4.0	4.0	9.5	9.8	12.5
w/accelerator	3.0	3.0	3.8	6.3	6.3	6.0
Temp. Rise Set (minutes)						
w/o accelerator	9.0	8.0	8.5	15.0	16.0	23.0
w/accelerator	6.0	5.5	8.0	11.0	13.0	11.0
Dry compressive strength	390 psi	618	--	400	490	440
Humidified 90°F/90% R.H. compressive strength	340 psi	490	--	370	450	400

*Allowed to hydrate at pH 2 in presence of excess sulfuric acid.

The above shows Portland cement and perlite additions at this one processing step lowered calcination temperature of the treated materials. The long unaccelerated set times of treated fluorostucco with some of the materials is not a significant problem because virtually all commercial gypsum board lines employ set control agents.

It has now been found that these contaminating ions can be rendered inactive in the solution phase, and then the gypsum which crystallizes out would be relatively free of impurities and have properties similar to natural gypsum. With sufficient treatment, the occlusion of these fluorine and aluminum ion species as the fluoroanhydrite is undergoing transformation to fluorogypsum can be prevented completely, and treatment in the calcination and/or gauging water hydration stages may not be necessary.

WHAT IS CLAIMED IS:

1. A process for the conversion of fluoroanhydrite to a hydrated calcium sulfate product which comprises

mixing a form of calcium sulfate from hydrogen fluoride manufacture with water and about 1-10 weight % of active siliceous material

and recrystallizing a hydrated calcium sulfate.

2. The process of Claim 1 in which the hydrogen fluoride manufacture calcium sulfate is fluoroanhydrite, and it is recystallized to fluorogypsum.

3. The process of Claim 1 in which the hydrogen fluoride manufacture calcium sulfate is fluorogypsum, and it is recrystallized to fluorostucco.

4. The process of Claim 1 in which the hydrogen fluoride manufacture calcium sulfate is fluorostucco, and it is mixed with gauging water to recrystallize a gypsum product.

5. The process of Claim 1 in which said siliceous material is Portland cement.

6. The process of Claim 1 in which said siliceous material is calcium silicate.

7. The process of Claim 1 in which said siliceous material is potassium silicate.

8. The process of Claim 1 in which said siliceous material is sodium silicate.

9. The process of Claim 1 in which said siliceous material is perlite.

10. The process of Claim 1 in which said siliceous material is pyrogenic colloidal silica.

11. The process of Claim 1 in which said siliceous material is diatomaceous earth.

12. The process of Claim 1 in which the hydrogen fluoride manufacture calcium sulfate is washed before being mixed with water and siliceous material.

13. The process of Claim 12 in which the calcium sulfate is washed with water.

14. The process of Claim 12 in which the calcium sulfate is washed with sulfuric acid.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US82/01776

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

US. CL. 423/555, 170; 106/109

INT. CL.3 C01F 11/46 C04B 1/06

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	423/170, 171, 172, 185, 555 106/77, 109, 110

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	U S, A, 3,847,634, VICKERY, 12 November 1974	1-14
Y	U S, A, 3,042,537, NEWELL, 03 July 1962	1-14
Y	U S, A, 3,547,581, GAUSTER ET. AL. 15 December 1970	1-14
X	U S, A, 2,606,127, WEBER, 05 August 1952	1-14
X	U S, A, 1,756,637, EDWARDS, 29 April 1930	1-6, 12-14
X	U S, A, 4,026,990, CZYSCH ET. AL., 31 May 1977	1-4, 10-11
A	U S, A, 1,969,449, BRYAN, 07 August 1934	1
X	G B, A, 983,204, FARBENFABRIKEN BAYER, 10 February 1965	1-6, 8

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] 16 March 1983	Date of Mailing of this International Search Report [2] 29 MAR 1983
International Searching Authority [1] ISA/US	Signature of Authorized Officer [20] Gary P. Straub

Form PCT/ISA/210 (second sheet) (October 1981)

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FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

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Y	G B, A, 1,174,512, OSTERRICHISCHE, STICKSTUFFWERKE AKTIENGESELLSCHAFT, 17 December 1969	1-14
Y	G B, A, 1,248,037, FISONS FERTILIZERS LIMITED 29 September 1971	1-14

V.☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.☐ Claim numbers.........., because they relate to subject matter [12] not required to be searched by this Authority, namely:

2.☐ Claim numbers.........., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

VI.☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]

This International Searching Authority found multiple inventions in this international application as follows:

1.☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.