

Destabilization of Sludge with Hydrolyzed Dasheen
Starch Flocculants

This invention relates to a novel hydrolyzed dash-
een starch composition and the process for making
5 and using the same. More particularly, this invention
relates to the discovery that dasheen starch which is
hydrolyzed in the presence of insoluble metal salts
formed in situ is a very effective flocculant in
destabilizing dilute as well as thick sludge suspen-
10 sions.

In general, the suspensions destabilized by the
starch composition of this invention are aqueous coll-
oidal suspensions containing either clay minerals or
metal oxides-hydroxides which are formed in large
15 volume during mining operations in the recovery of
materials such as coal, bitumen from tar sands and
metals, and such suspensions are also formed in paper-
making operations. In the case of metal mining oper-
ations, suspensions known as slimes are formed, typ-
20 ically phosphate slimes or like materials produced
in the mining of copper, nickel, and titanium. In
coal and tar sands minings, for example, the mining
effluent typically contains dilute or thick clay
mineral suspensions. In paper-making processes cell-
25 ulosic fines, clays and other solids are present in the
large volumes of liquids obtained.

In order to properly dispose of these voluminous

mining discharges, regardless of their source, flocculants have conventionally been employed to destabilize these suspensions and thus permit the effective separation of water from solids. The use of wheat, corn and potato starch which has been hydrolyzed in the presence of metal salts formed in situ has been disclosed in U.S. Patent No. 4,289,540 which issued on September 15, 1981. It has now been found that surprisingly superior flocculation is obtained if starch from the root of the dasheen plant is used for preparing the hydrolyzed starch composition to give the starch flocculant.

It is, therefore, an object of this invention to provide an effective flocculant in destabilizing dilute as well as thick sludge suspensions, particularly colloidal suspensions obtained from mining operations.

It is a further object of our invention to provide an effective flocculating agent for treating tar sands tailing streams which carry suspended clay particles.

It is another object of our invention to provide such a flocculating agent which is economical to prepare and employ in the treatment of both tar sands tailing streams, and phosphate slimes obtained from phosphate mining operations.

In another aspect, it is yet another object of our invention to provide such a flocculant which is safe and easy to handle and which itself offers no

ecologically undersirable side effects.

In accordance with the present invention, it has been found that the foregoing and other objects may be achieved by employing a hydrolyzed dasheen starch as a flocculant in destabilizing dilute as well as thick sludge suspensions. More particularly, it has been found that when these starches have been hydrolyzed in the presence of metal salts formed in situ there is formed a surprisingly effective composition for destabilizing such suspensions. Still more particularly, an especially effective flocculant composition may be prepared when calcium alumino phosphate dasheen starch is used.

As aforestated, the sludges being treated in accordance with this invention are aqueous colloidal suspensions containing either clay minerals or metal oxides-hydroxides which are formed during mining operations or other operations generating such suspensions. For sake of illustration and simplicity only, the following description will be directed to a colloidal clay suspension obtained from bituminous tar sands mining. However, it will be understood that this invention is directed generally to the destabilization of all such suspensions.

As aforementioned, the flocculant is prepared from a dasheen starch which has been hydrolyzed in the presence of inorganic salts formed in situ.

The dasheen starch itself is readily obtained from the dasheen plant which is the common name for the plant Colocasia esculenta, including the variety antiquorum (taro). The plants are among the few

5 edible members of the aroid family (Ayaceae) and are native to South-eastern Asia and Malaysia. The edible corms (underground stems) from which the starch is obtained support a cluster of large leaves 4 to 6 feet (1.2 to 1.8 m) long often called elephant's ears.

10 Separation of the dasheen starch from the root is well known in the art and need not be repeated in detail here. However, for the sake of completeness, the dasheen starch used in the examples which follow was obtained in the following manner:

15 To 15 pounds (6.8kg) of the peeled, diced dasheen corms 1.5 gallons (5.7 litres) of water was added to which 15 gms of potassium metabisulphite had also been added to prevent discolouration. The mixture was chopped with water in a blender at low speed just

20 long enough to break up the cells (approximately 2 mins.) Then, the mass was filtered through a No. 60 mesh (250 micrometres) filter to remove the fibrous material from the starch suspension. The fibrous material was washed twice with fresh quantities of water

25 and the starch suspensions combined and allowed to settle. Finally, the water was decanted and the starch was dried in an oven at 60°C or sun-dried after which

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time it was ready for use.

The hydrolysis of the dasheen starch is achieved by simply heating the starch in the form of an aqueous suspension at about 85° to 95°C and preferably at about 90°C in the presence of soluble metal salts which will form an insoluble salt in situ. The starch should desirably be present in an amount of 1 gm to 10 gm per 100 ml of water, and preferably 2 to 6 gms per 100 mls of water.

Among the salts which may be employed during the hydrolysis are salts of metals such as sodium, potassium, ammonium, magnesium, calcium and aluminium. The respective anions may be sulphates, acetates, chlorides, nitrates, chlorates, bromides, iodides, thiocyanates, phosphates and the like. Particularly effective for purposes of this invention, as applied to tar sands tailing ponds, is calcium alumino phosphate dasheen starch, although such other salts containing sodium, aluminium and phosphate ions and the like may also be used.

As indicated, the salts are added as soluble salts in order to form the insoluble salt in situ. Thus, for example, the preferred calcium alumino phosphate salt is advantageously formed in situ by the addition of specified amounts of calcium hydroxide, aluminium sulphate, and sodium phosphate to the aqueous dasheen starch hydrolysis medium. In any event, the resulting

salt should desirably be present in amounts of about 10 to 30 gms per 100 gms of starch, and preferably 15 to 20 gms per 100 gms of starch.

5 In the case of treatment of known phosphate slimes from phosphate mining operations with the flocculant of this invention, it will be understood that the presence or addition of a phosphate, such as sodium phosphate, is not necessary and may be omitted from the salt preparation.

10 If desired, the dasheen starch hydrolysate may be treated to remove water; e.g. drying by freeze-drying, air-drying, spin-drying or the like, to provide a powder which is convenient to handle, store and transport, yet which can be readily redispersed in water
15 at the treatment site.

The following Examples are provided for purposes of illustrating but not limiting the scope of this invention with respect to the preparation and use of the starch flocculants.

20 SYNTHESIS OF HYDROLYZED DASHEEN STARCH FLOCCULANT

Five grams of dasheen starch is weighed into a flask fitted for refluxing. Two hundred millilitres of aqueous solution containing 0.617 gm of $Al_2(SO_4)_3 \cdot 18H_2O$, 0.704 gm $Na_3PO_4 \cdot 12H_2O$, and 0.463 gm $Ca(OH)_2$ are
25 added to form calcium alumino phosphate in situ in the presence of the starch.

The suspension is refluxed at $90^\circ C \pm 5^\circ$ for two hours

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with simultaneous stirring. The hydrolysis is considered complete when the insoluble starch is converted into a colloidal solution. The volume is then made up to 250 ml with distilled water, thus giving
5 a stock solution of 20,000 ppm of calcium aluminium phosphate dasheen starch.

A preferred procedure for making the hydrolyzed dasheen starch employs the method described in U.S. Patent application S.N. 327,850, filed December 7, 1981.
10 In the preferred method, an aqueous suspension of the starch alum and lime is heated until maximum viscosity of the suspension is obtained, and immediately thereafter the salt to be added (e.g. trisodium phosphate) is added to the mixture. The general procedure for such
15 preferred method is as follows:

To 2.67 litres of tap water add 109.89 g dasheen starch, 10.18 g lime and 6.78 g alum and heat the mixture with stirring at a constant speed of 100 rpm at a rate of 0.5°C per minute. Stirring is carried
20 out with a Cole-Palmer Master Servodyne torque stirrer calibrated to give viscosity value. As heating and stirring are continued the viscosity is observed to rise significantly when a temperature of about 60°C is reached and continues to rise until about 70°C is
25 reached, at which point it begins to fall and then 15.46g of trisodium phosphate (Na_3PO_4) is immediately added.



Heating and stirring at the same rate is continued until a temperature of 85° is reached, and then the heat is removed and the material is allowed to cool to room temperature. This hydrolyzed dasheen starch suspension containing about 4% of the starch composition was used in the comparative tests which follow.

COMPARATIVE EXAMPLES

In order to compare and evaluate the efficiency of the dasheen starch flocculants as settling aids, the test flocculants were used to treat tar sand tailings.

The tar sand tailings used contained 1.93% solids (w/w) which are largely silts and clays. The fines are quite dispersed and tend to remain in suspension for a long period of time.

Settling Tests of Tar Sand Tailings Treated With Starch Flocculants

100 ml of the tar sand tailings were poured into a 100 ml cylinder and then 0.1 ml of alum (0.06m-mole/l) was added to the tailings sample. The cylinder was inverted 5 times to mix the tailings with the alum. Then 0.25 ml of the 4% hydrolyzed dasheen starch flocculant suspension was poured into the cylinder. The cylinder was again inverted five times. The dosage of treatment is approximately 100PPM. The same procedure was used for a hydrolyzed wheat starch flocc-

ulant used for comparison. The treated samples were then allowed to settle in the cylinders without further disturbance. The sediment heights were recorded periodically until little change was observed.

5 Kynch Analysis of the Settling Tests

Results of the settling tests were evaluated in terms of Kynch analysis which gives a settling time called "Ultimate time" (T_u). T_u is an indicator of the duration required for a sediment to reach close to the ultimate height and this parameter is used to evaluate the efficiency of settling aids in suspensions.

Another parameter for the expression of settling efficiency of sediments is called "Unit Area" which is defined as follows:

15

$$\text{Unit Area} = \frac{T_u}{C_o \times H_o}$$

20 where C_o = initial solids concentration (ton/cu. ft) (t/m^3)

H_o = initial height (ft) (m)

T_u = ultimate time (days)

25 Unit Area is expressed as sq. ft/ton/day ($m^2/t/day$). This is the area required to settle one ton (t) of solids per day. Small Unit Area indicates efficient settling. The T_u and unit areas of the hydrolyzed

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dasheen starch flocculant treated samples, a hydrolyzed wheat starch flocculant treated sample and an untreated sample are presented in Table I.

TABLE I

Tar Sand Tailings Treated With Flocculants

	<u>T_u (Min)</u>	<u>Unit Areas</u> <u>sq. ft/ton/day</u> <u>(m²/t/day)</u>
10		
Untreated	1440	248.63 (29.15)
Hydrolyzed Wheat Starch Flocculant*	98	191.73 (19.63)
15		
Hydrolyzed dasheen Starch Flocculant*	40	78.27 (8.02)

* Prepared by the preferred
method of S.N. 327,850

20 As can be seen from the above table the hydrolyzed dasheen starch flocculant of the invention is surprisingly superior to the hydrolyzed wheat starch flocculant.

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CLAIMS:

1. A process for the destabilization of colloidal sludge suspensions containing clay minerals or metal oxides-hydroxides, which comprises treatment of said suspensions with a flocculating reagent to substantially separate water from suspended solids, the flocculating reagent being a hydrolyzed dasheen starch obtained by the aqueous hydrolysis of the starch in the presence of at least one insoluble metal salt formed in situ.

2. A process according to claim 1 wherein the sludge suspension is derived from bitumous tar sands mining operations.

3. A process according to claim 1, wherein the sludge suspension is a phosphate slime obtained from phosphate mining operations.

4. A process according to any of claims 1 to 3, wherein the hydrolyzed starch is calcium alumino phosphate dasheen starch.

5. A process according to any of claims 1 to 4, wherein the concentration of flocculating reagent in the sludge suspension is controlled to provide at least 50 parts per million.

6. A composition comprising a hydrolyzed dasheen starch obtained by the aqueous hydrolysis of dasheen starch in the presence of at least one insoluble metal salt formed in situ.



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7. A composition according to claim 6, wherein the salt contains calcium, aluminium and phosphate ions.

8. A composition according to claim 6 or 7, wherein the aqueous hydrolyzed starch is dried to form a solid

5 composition.

9. A process according to claim 1, substantially as hereinbefore described with reference to any of the Examples.

10. A composition according to claim 6, substantially
10 as hereinbefore described with reference to any of the Examples.
