

DESTABILIZATION OF SLUDGE WITH HYDROLYZED CASSAVA STARCH
FLOCCULANTS

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

In general, the suspensions destabilized by the
starch composition of this invention are aqueous colloidal
suspensions containing either clay minerals or metal
oxides-hydroxides which are formed in large volume
15 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 operations, suspensions known
as slimes are formed, typically phosphate slimes or like
20 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
cellulosic fines, clays and other solids are present
25 in the large volumes of liquids obtained.

In order to properly dispose of these voluminous
mining discharges, regardless of their source, floccul-

ants 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
5 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 cassava plant is used for preparing the
10 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
15 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
20 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
25 invention to provide such a flocculant which is safe and easy to handle and which itself offers no ecologically undesirable 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 cassava 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 cassava 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 cassava starch which has been hydrolyzed in the presence of inorganic salts formed in situ.

The cassava starch itself is readily obtained from the cassava plant which is a tropical plant having swollen roots which store the starch. The cassava plant

(12)

is also known as Manioc (Manihut utilissima), family Euphorbiaceae and in some areas is referred to as yucca ("Starch - Its Sources, Production and Uses", Charles A. Brantleht, Reinhold Publishing Corp., 1953).

5 Separation of the cassava 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 cassava starch used in the examples which follow was obtained in the following manner:

10 To 15 pounds (6.8kg) of the peeled, diced cassava root 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 long enough to
15 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 and the
20 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 time it was ready for use.

The hydrolysis of the cassava starch is achieved
25 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

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- 5 -

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 cassava 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 advantageous formed in situ by the addition of specified amounts of calcium hydroxide, aluminium sulphate, and sodium phosphate to the aqueous cassava 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.

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

(14)

or addition of a phosphate, such as sodium phosphate, is not necessary and may be omitted from the salt preparation.

5 If desired, the cassava starch hydrolysate may be dried to remove water by freeze-drying, air-drying spin drying or the like, to provide a solid powder composition which is convenient to handle, store and transport and which can readily be redispersed in water at the treatment site.

10 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.

— 15 SYNTHESIS OF HYDROLYZED CASSAVA STARCH FLOCCULANT

Five grams of cassava starch are weighed into a flask fitted for refluxing. Two hundred millilitres of aqueous solution containing 0.617 gm of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, 0.704 gm $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, and 0.463 gm $\text{Ca}(\text{OH})_2$ are
20 added to form calcium alumino phosphate in situ in the presence of the starch.

The suspension is refluxed at $90^\circ\text{C.} \pm 5^\circ$ for two hours with simultaneous stirring. The hydrolysis is
25 considered complete when the insoluble starch is converted into a colloidal solution. The volume is then made up to 350 ml with distilled water, thus giving a stock solution of 20,000 ppm of calcium aluminium

phosphate cassava starch.

A preferred procedure for making the hydrolyzed cassava starch employs the method described in U.S. Patent application S.N. 327,850, filed December 7, 1981. 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 preferred method is as follows:

To 2.67 litres of tap water add 109.89 g cassava 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 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 reached, at which point it begins to fall and then 15.46 g of trisodium phosphate (Na_3PO_4) are 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 cassava 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 cassava starch flocculants as settling aids, the test flocculants were used to treat tar sand tail-
5 ings.

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.

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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 (0.06 m-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 cassava starch flocculant suspension was poured into the cylinder. The cylinder was again inverted five times. The dosage of treatment is approximately 100 PPM. The same procedure was used for a hydrolyzed wheat starch flocculant used for comparison. The treated samples were then allowed to settle in the cylinders without further disturbance. The sediment heights were recorded periodically until
25 little change was observed.

(17)

- 9 -

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:

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

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

H_o = initial height (ft) (m)

T_u = ultimate time (days)

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Unit Area is expressed as sq. ft/ton/day ($m^2/t/day$).

This is the area required to settle one (t) of solids per day. Small Unit Area indicates efficient settling.

The T_u and unit areas of the hydrolyzed cassava starch flocculant treated samples, a hydrolyzed wheat starch flocculant treated sample and an untreated sample are presented in Table 1.

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(18)

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>
Untreated	1440	284.63 (29.15)
Hydrolyzed Wheat Starch Flocculant*	98	191.73 (19.63)
Hydrolyzed Cassava Starch Flocculant*	49	95.73 (9.80)

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

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



- 11 -

CLAIMS:

1. A process for the destabilization of colloidal
sludge suspensions containing clay minerals or metal
5 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 cassava starch obtained by
the aqueous hydrolysis of the starch in the presence
10 of at least one insoluble metal salt formed in situ
2. A process according to claim 1, wherein the sludge
suspension is derived from bituminous tar sands mining
operations.
3. A process according to claim 1, wherein the sludge
15 suspension is a phosphate slime obtained from phosphate
mining operations.
4. A process according to any of claims 1 to 3, where-
in the hydrolyzed starch is calcium alumino phosphate
cassava starch.
- 20 5. A process according to any of claims 1 to 4, where-
in 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 cassava
25 starch obtained by the aqueous hydrolysis of cassava
starch in the presence of at least one insoluble metal
salt formed in situ.



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- 12 -

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 composition.
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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 as hereinbefore described with reference to any of the Examples.
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