INVESTIGATION OF SOLID PHASE STARCH MODIFICATION REACTIONS

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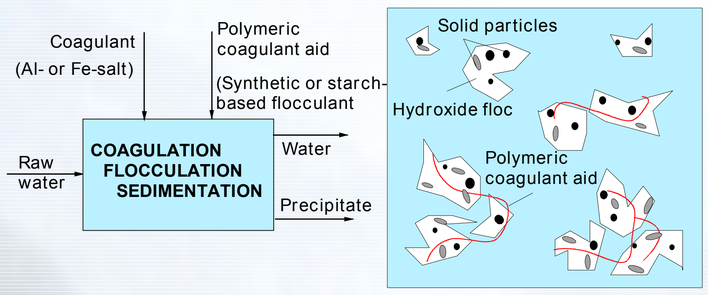
Flocculation in the water treatment

Flocculants: polyelectrolytes – water soluble polymers with ionic charge. They can agglomerate the colloids in aqueous suspensions by neutralising the charges of the particles and by bridge-forming. Today the flocculants used in the industry are mostly synthetic products (polyacrylamide, polyethylene-oxide, etc.). These are very effective, but may contain toxic monomer residuals and they are not biodegradable.

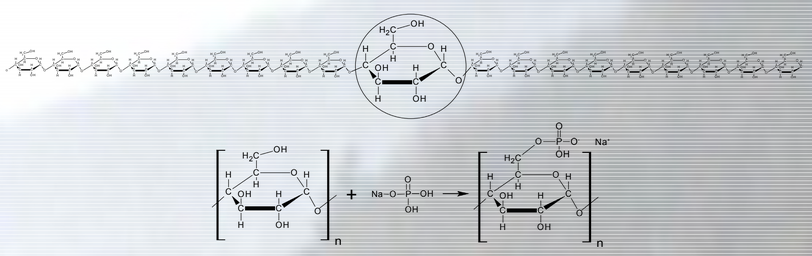
Flocculation in the drinking water treatment: in the clarification (coagulation + sedimentation) step anionic flocculants are used. Al^{3+}- or Fe^{3+}-salts are added to the water to be treated, and polyelectrolytes improve the sedimentation of the forming flocs by linking them.



Environment-friendly starch based flocculants

Native starch is a mixture of polymers of molecular weights ranging from 5O,OOO to hundred millions. It is not water-soluble.

Idea: Starch can be converted into flocculants by substituting some of the OH^--groups in the anhydroglucose monomer units with ionic functional groups. Anionic flocculants can be produced by building phosphate groups into the polymeric chains if the polymeric structure of the starch is preserved.



The starch derivatives if produced with the proper reagents are non-toxic and indeed biodegradable. The objective then is to produce natural based flocculants for those fields where their beneficial properties are really an advantage. Such a field is drinking water treatment.

Preparation of starch based flocculants in the laboratory

Solid phase reaction: Native starch is impregnated by the solution containinig the reagents, followed by drying and heat treatment at 140-150 °C.

Experiments: The object of the laboratory scale experiments is to find the best composition and the optimal reaction parameters: temperature and duration of heat treatment.

Equipment: mortar and oven (or block heater).

Evaluation of the derivatives: flocculation efficiency: kaolin test and jar tests according to the application.

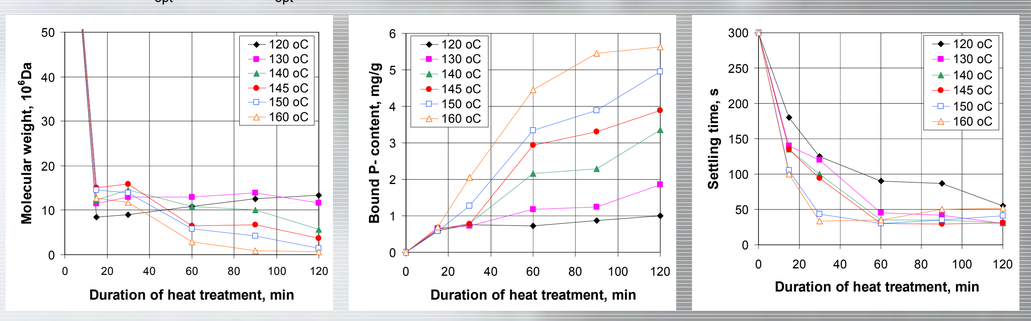
Sedimentation of 5 g/dm^3 kaolin suspension without and with 10 ppm starch based flocculant

Investigation of starch modification reactions in the laboratory

Flocculation efficiency: enhanced by (a) molecular weight, (b) ionic charge and (c) water solubility.

Modification: parallel reactions:
(a) degradation of polymers → lower molecular weight → better water solubility
(b) building in of PO_4^{3-} -groups → increased ionic charge → better water solubility

Result: optimal reaction parameters were found for the laboratory scale modification:
T_{opt} = 145 °C, t_{opt} = 90 min



Changing of the properties of starch derivatives during the modification

Production of anionic flocculant in the pilot plant

Reactor: batch type multifunctional reactor: all steps of the modification are carried out here.

Capacity: 100 kg/charge
Reactor volume: 0.45 m^3
Vacuum pump, condenser
Spraying: pneumatic nozzle
Mixing: horizontal impeller
Heating: electric heating mantel
with temperature control

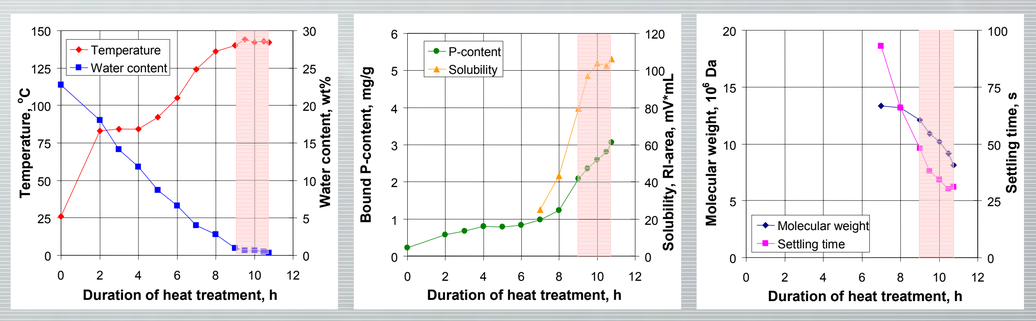
During the drying and heat treatment the temperature is changing continuously. The reaction can take place in the drying period too.

Modification of starch in the pilot plant

Problem aroused in the pilot plant: because of the lower heating capacity/mass rate the drying period in the pilot scale reactor takes about 9 hours, while in the laboratory experiments it takes ~5 minutes.

How can we determine the heating program and the endpoint of the modification?

(a) clearing up the kinetics of drying
(b) clearing up the kinetics of phosphorylation and degradation reactions



Changing of the properties of starch derivatives during the modification

Application of the starch based anionic flocculant

One of the starch phosphate derivatives was registered by the name of Greenfloc 213A and the Hungarian authorities allowed its use in the drinking water treatment.

The amount of flocculant produced in the pilot plant made possible industrial scale experiments. The experiments at the Waterworks of Lazberc proved that our flocculant is suitable for the substitution of synthetic agents in the coagulation-flocculation step of water treatment.

Water characteristics measured:

turbidity removal,
algae removal,
DOC removal,
residual coagulant,
residual coagulant aid,
total organic carbon.

The Waterworks of Lazberc started working with this starch based flocculant two years ago alternately with synthetic flocculants (depending on the raw water quality). At similar dosage of flocculants the characteristics of the produced water are usually better than before.

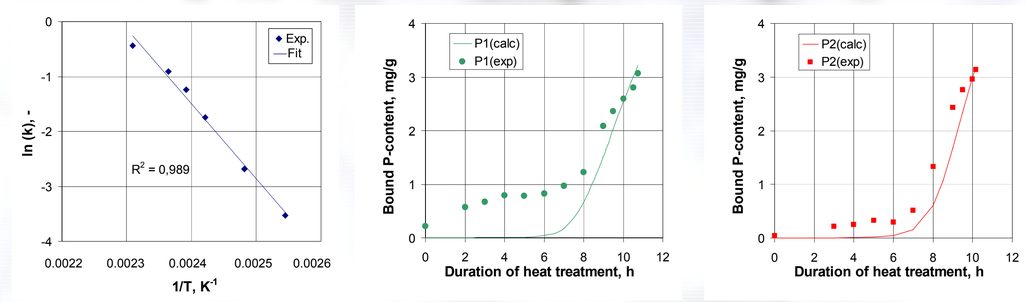
Kinetics of the phosphorylation reaction

Kinetic parameters were determined based on the laboratory experiments. Starch phosphates were prepared at 120-160 °C and 15-120 min, and bound P-contents of the samples were analysed.

Provided that the reaction is characterised by first order kinetics, the reaction rate constants (k) were determined as a function of the temperature (T).

From the Arrhenius equation
$k_\infty = 4.17\ 10^{13}\ h^{-1}$
$E_a = 1.14\ 10^5\ J\ mol^{-1}$

Using the kinetic parameters and the measured temperatures in the pilot scale reactor we have calculated the expected concentrations (calc) and compared them to the measured values (exp).



These results will help us at the scaling-up to a full scale reactor.