Physics. — The clarification of coal-washery effluent. By F. K. Th. VAN ITERSON.

(Communicated at the meeting of January 29, 1938.)

1. Introduction.

In "Separation of Substances by Flotation" we described 1) the coalslurry flotationplant of the State Mines in Limburg (Holland) and announced, that the treatment of the tailings, a dark grey liquor, containing about 3 percent of suspended solids consisting of shale particles and other dirt, partly in colloidal dispersion, would be the subject of a subsequent communication.

The treatment of this effluent, which is dealt with in the present paper, is of a principally chemical character.

Although the use of chemicals for the purification of industrial effluent was a well established method of sewage treatment already some 60 years ago and chemical precipitation has been discussed in detail for many years 2), the application of coagulants for the clarification of coal-washery effluent has become economically feasible only in recent years.

Formerly the transport, storage and removal of the flocculated sludge offered the most serious problem in connection with the chemical treatment of sewage and industrial effluent. The freshly precipitated sludge had a watercontent of 80—95 percent, the cost of transport over long distances was prohibitive and it could not be deposited on the land or dumped without causing justified complaint.

Two inventions brought about the practical appliance of clarification by flocculation:

- 10. The development of the rotary-vacuum filters of the Oliver-, Wolff- and Rovac-type, which have made it possible to obtain a cake, that can be easily transported and dumped, or dried and incinerated.
- 20. The use of prepared starch as precipitant in stead of alum, ferrous sulphate (copperas), ferricchloride, lime, sulphuric acid or other electrolytes, which add weight to the sludge and make it very bulky.

Before describing some results of the elaborate research work carried out by the State Mines, a short paragraph may give an outline of the importance of chemical flocculation in engineering. An allied subject of

¹⁾ Proc. Royal Netherlands Acad. Amsterdam, 40, 93, 228 (1937).

²) The most complete article on chemical treatment of sewage appeared in: Sewage Works Journal, Vol. VII, No. 6, Nov. (1935), p. 997. The bibliography enumerates 249 publications on the subject. The newer literature not given in that report is noticed at the end of this communication.

colloid chemistry of equal interest for the technician is peptization, but this cannot be dealt with now.

2. Chemical Flocculation.

a. When acids, bases and salts are dissolved in water their molecules are immediately, more or less completely dissociated by the water into electrically charged ions. Thereby one or more electrons pass from the atoms of the electropositive element to the electronegative part of the electrolyte-molecule. In water, with its high dielectrical constant this tendency results in the more or less complete dissociation of the electrolyte molecule in its anion and cation. The anions carry away one or more surplus electrons and therefore obtain a negative charge, the cations deprived of these electrons are positively charged. In the same way water itself is slightly dissociated. Pure water contains $\frac{1}{10^7}$ grams $=\frac{1}{10^4}$ mg H⁺

(cation) and
$$\frac{17}{10^4}$$
 mg OH⁻ (anion) per litre.

- b. The most important characteristics of colloidally dispersed matter are the result of their tendency to carry electrical charges, so that there is a potential difference between the particles and the surrounding medium and a repellent force between the particles themselves. Colloidal suspensions of clay, kaolin, quartz and carbon carry a negative charge, colloidal dispersions of metalhydroxydes carry positive charges. Gelatine is slightly positive in acid, negative in alkaline solutions. The source of these charges may be explained by the splitting off of ions from the "colloid" or by the absorption of ions by the "colloid" from the surrounding medium.
- c. Substances in the colloidal state are readily precipitated by the addition of electrolytes. This phenomenon is associated with the neutralisation of the charge on the "colloid"-particles.

In 1887 C. LELY figured that the weight of the mud yearly carried to the sea by our great rivers, the Rhine and the Maas, amounts to 3 million m^3 . The clay particles, mostly smaller than 100 μ , many of colloidal fineness, all negatively charged, repulse each other and show little tendency to settle in fresh water. But as soon as the water is mixed with seawater their charge is neutralised by the absorption of Na+, Mg++ and Ca++ ions and flocculation takes place. The divalent cations Mg++ and Ca++ may have a flocculation power about 75 times greater than the monovalent Na+ and K+ cations 1).

Our country has originated from the chemical flocculation of river dirt 2), and in the same way other fertile lands, the delta of the Nile, the plains of the Po and Mississippi etc. have been deposited.

¹⁾ H. FREUNDLICH, Kapillarchemie, 4 Aufl. (1932) II Band, S. 120. KRUYT, Phys. Chem., 6de druk (1936), p. 138.

²) J. VAN BAREN, De Bodem van Nederland, Deel II (1927), p. 778, was the first to apply the principles of colloid-chemistry for explaining geological processes.

Mischances arose from overlooking this phenomenon, we mention the silting up of large storage reservoirs, obtained by building dams through river-valleys 1).

In our own country and elsewhere many costly engineering failures occurred, which are the consequence of neglecting the basic laws of "colloid"-chemistry 2). It took a long time before it was realised that the formation of the bars at river mouthes can only be prevented by dredging. And even to day when model-experiments are carried out on the silting of tidal harbours, the main source of settlement is disregarded 3).

d. Besides the treatment of sewage and industrial effluent, many other technical applications of flocculation can be mentioned. BUSWELL 4) discusses at considerable length the mechanism of purification reactions envolved with the use of aluminum-salts at filtration-plants for domestic water supplies.

The same principle is applied in the treatment of the condensates of steam-engines containing some oil in emulsion, which is successfully treated by flocculating agents, according to the invention of Dyxhoorn (applied at the Steam Pumping Drainage plants Lemmer and Vollenhoven) 5).

Well known, from antiquity, is the use of white of eggs for the clarification of the best sorts of claret and of gelatine for the cheaper wines.

Prepared casein is used in the china (earthenware) industry in order to precipitate kaolin from its dispersion.

The largest employment of flocculating reagents is made in the dye-stuff industry and for ore-dressing ⁶).

3. Practical aspects of flocculation for the treatment of washery water, especially in the Limburg coal district.

The particle-size of the solids suspended in the washery-water of

¹⁾ Silting of four large reservoirs in South Africa, by Lewis. Second Congress on Large Dams, Washington D.C. (1936), p. 15. Salinity and Flocculation. The passage of turbid water through Lake Mead. by GROVER and HOWARD. Proc. Am. Soc. of Civil Engineers, 63, 643—667 (1937).

²⁾ Every engineer should study: KRUYT, Inleiding Phys. Chemie (Kolloidchemie), Amsterdam, Colloid, New York.

³) The United States Waterways Experiment Station at Vicksburg. Engineering, II, p. 193, 250, 273, 361 (1937).

Modellversuche für Tideflüsse von R. SEIFERT, Zeitschrift des Vereins deutscher Ingenieure, 2 October, S. 1161 (1937).

⁴⁾ A. M. BUSWELL, Chemistry of Water, p. 160-177 (1928).

⁵) TAGGART in Handbook of Ore Dressing, mentions: Ellis working with positive hydrate of ironcolloid and negative cylinder-oil emulsions. (Too much Fe(OH)₂ gives dispersion).

⁶) Handbook of Ore Dressing by A. F. TAGGART, New York. JOHN WILEY SONS (1927). Thickenig 4, Flocculation, p. 974.

coal mines varies from a few millimeters to some ultramicrons. The colloidally dispersed matter passes through filterpaper.

These solids include coal as well as the minerals associated with it, the most common of these being shale (clay), pyrites and calcite. These suspended solids may be classified into particles which being large enough to settle rapidly, are dealt with by mechanical means, i.e., settling tanks, slurry shakers or other devices, and particles which are so small that they require flocculation. Usually it is not possible to use sieves with a smaller aperture than $\frac{1}{2}$ mm and this fixes the maximum size of particle which enters into flocculation.

The problem to be handled by the anthracite collieries, (the private mines in the Limburg district), differs from that to be dealt with by the three largest State Mines in so far, that the former have to treat washery water, charged with fine coal particles, which after precipitation form a sludge that can be sold as an excellent and cheap fuel for domestic use, while the washerywater of the three bituminous coalmines is already stripped of all coalparticles by the froth flotation process but contains a considerable quantity of tailings which form a burdensome sludge of no value at all.

This explains why the private mines in Limburg were the first to clarify their washery effluent.

There are three different principles, by which matter in suspension and in colloidal "solution" may be deprived of its electrical charge, so that it may gather in flocs and settle.

a. Flocculation by electrolytes.

Hydrate of lime is used with great success at the private mine "Oranje-Nassau" at Heerlen for the precipitation of coal slurry (dutch "kolenslik", german "Schlamm") and at State Mine Maurits for the clarification of the joint effluent, containing some coal particles but mostly shale ranging from colloidal fineness to dimensions of about 20 μ .

Formerly when this water was delivered untreated into the Keutelbeek, this stream was black like ink. Now the Keutelbeek, over a certain part of its course, is white like milk. The explanation of this rather curious phenomenon is simple. The effluent which is discharged into the stream is clear, but in order to meet irregularities a small excess of hydrate of lime is added. The stream itself is polluted by sewerage in state of biological oxydation and steadily develops CO_2 , which first precipitates the lime and then in the course of a mile or so dissolves it as $CaH_2(CO_3)_2$.

The figures 1, 2 and 3 show how the precipitated sludge is dug, conveyed and dumped at present. This way of dealing with the effluent is too expensive and a part of it still escapes untreated.

Other commonly used electrolytes for flocculation, such as iron- and aluminum-salts act differently according to the alkalinity of the water. The effluent of the coal mines of Limburg is definitely alkaline. Therefore the flocculation with iron-salts is not caused by the ferrous or ferric ions

F. K. TH. VAN ITERSON: THE CLARIFICATION OF COAL-WASHERY EFFLUENT.



Fig. 1. Precipitation and settling ponds of effluent at Statemine Maurits. Transporting bridge with bucket dredger and elevator at background.



Fig. 2. Detail-view of bucket dredger, rubber-belt conveyor and elevator for charging dumping cars with sludge flocculated with lime.

Proceedings Royal Netherlands Acad. Amsterdam, Vol. XLI, 1938.



Fig. 3. Dumping of flocculated sludge. See cracks in dried material in foreground.

but by colloidally dispersed hydroxydes. Ferric salts have no advantage as they are readily reduced by the effluent.

b. Flocculation by "colloids" with an electric charge of opposite sign. Cataphoresis of the suspension, (the migration of the particles in an electric field) shows that fine particles of coal and clay dispersed in the washery water carry a negative electric charge, whereas colloidally dispersed ironhydroxydes are positively charged.

Mr. TROMP, chief chemist of the Domaniale Mijn (a private mine at Kerkrade) ascertained, that under the conditions prevailing at that colliery, the most economical way of precipitating the solids is by the use of ferrous sulphate (Fe_2SO_4 7 aq).

Some sulphuric acid added to the crystals in the dissolving tank, prevents the formation of $Fe(OH)_2$. In the very dilute and slightly alkaline solution prevailing in the settling pond, precipitation of the coal particles is caused by neutralising the negatively charged particles of coal by positively charged colloidal ferrous hydroxyde and the subsequent sweeping of the suspension by the settling flocs.

c. Flocculation by starch.

The third and by far the most important manner by which the greater part of the electric charge of the suspended matter in washery effluent can be carried away, so that large flocs are formed, is the addition of a very weak "solution" of starch.

The precurser of this method was the Henry-process, in which lime and frozen potato starch treated with caustic soda was used.

In the Limburg-mining district this process was first applied with a perfect success at the private mine "Willem Sophia" at Spekholzerheide. Generally the Henry process is too complicated and too expensive. But in this particular case, where a small quantity of effluent was treated and the clear water could be recirculated infinitely, it still was a profitable process.

The literature on the Henry-process is extensive 1).

In later years exhaustive experiments carried out in the laboratories of the State Mines in Limburg have definitively shown that the addition

¹⁾ Klaringsinstallatie van het Afvalwater van de mijn "Willem Sophia", Geologie en Mijnbouw, 10, 74 (1931).

Neuartiges Waschwasserklärverfahren im Steinkohlenbergbau, von G. GRÄF, Hamborn. (Mitteilung aus dem Ausschuss für Steinkohlenaufbereitung Glückauf, 68, 304 (1931).

The Henry-Process for the Clarification of Polluted Water, Engineering 138, 213, 293 (1934) and 142, 607 (1936).

Betriebsversuche zur Klärung von Schlammwasser aus der Steinkohlenwäsche von Dr. Ing. W. PETERSEN, Glückauf, 70, 125 (1934).

PETERSEN writes: "Das nach HENRY behandelte gefrorene und in Sodalösung gequollene Kartoffelmehl hatte keine bessere, sondern verschiedentlich sogar eine schlechtere Flockung der Schlämme als die gewöhnliche Stärkelösung zur Folge."

Revue Universelle des Mines. Recherches sur les Colloïdes, par A. GILLET. Tome XI, No. 5, 118 (1935).

of relatively large quantities of lime is a serious drawback of the Henry process; it was shown that there is no real advantage to be gained by freezing the starch and that the specially prepared soluble starches, which are now available, are more economical and easier to deal with; moreover they don't decay nor loose their flocculating power so quickly as ordinary boiled potato flour. The mine "Willem Sophia" now uses Flocgel of W. A. Scholten's Chemische Fabrieken N.V., Groningen (Holland), which is to be considered as a very effective coagulant. It is largely exported for flocculation devices.

Other types of starches, especially manufactured for the same purpose, are:

Mogul, a corn starch with 4 percent of protein, which is used at the Champion Mine of the Pittsburgh Coal Company, Pittsburgh Pa. (We received a sample from Mr. J. B. Morrow, Preparation Manager of this Company).

Ogwen Powder which can be obtained from Bagshaw & Bruce, Amberley House, Norfolk Street, London W.C. 2.

Unifloc being a soluble gel, and therefore easy in application, to be obtained from Unifloc Reagents Limited Swansea, 10 Adelaide Street.

B. 4. An excellent, but somewhat expensive liquid starch, very easy to employ, sold by International Combustion Ltd., Aldwych House, Aldwych, London W.C. 2.

But the most wonderful product of this kind is:

Konyaku flour, a japanese starch, obtained from the root of Amorphopallus Rivieri, with 30 percent mannane.

Figure 4 shows the superiority of Konyaku flour over potato starch.

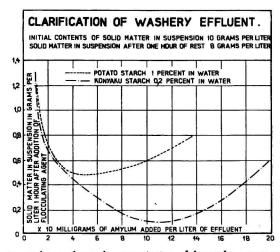


Fig. 4. Tests made to show the superiority of konyaku- over potato-starch.

The amount of prepared starch required to clarify a thick suspension of dirty water is very small and the adsorbtion of the starch is complete.

The sludge is much more compact than when electrolytes are used, so that it is not astonishing how these products find a rapidly increasing market.

4. Theoretical explanation of the clarification of washery effluent by starch "solutions".

The behaviour of prepared starch as a flocculating agent differs in many respects from that of electrolytes.

- 1. The molecular weight of starch $(C_6H_{10}O_5)$ is many hundreds times greater than the weight of the ions used for neutralising the charge of coal- or clay-particles, and the total weight of flocculant is about 10 times less, which indicates that a starch molecule has a remarkably individual action.
- 2. A certain retardation in the action of starch solution is observed, while the action of electrolytes at the most favourable concentration is instantaneous.
- 3. Electrolytes coagulate colloidally dispersed solids, while starches (in the absence of electrolytes) preferably precipitate the coarser particles.
- 4. Coal- and particularly clay-particles in washery effluent carry a definite negative charge. The most striking difference in behaviour between starch and electrolytes is in the way by which this charge is removed.

With electrolytes the absorbed ions of opposite sign neutralise the charge of the "colloidal" particles.

The starch micelles, brought into the washery-effluent are slightly charged negatively and still this mysterious molecule is able to discharge coarse particles of coal and shale.

According to Holleman—Wibaut 1) the molecule of amylum is supposed to consist of a long open chain of rests of maltose, composed of linked rings attached to each other in the same way as are the two rings of maltose, which is an α -glucoside of β -glucose 2).

The formulae given in figure 5 show how by the elimination of H_2O maltose and starch molecules are built up from β -glucose ($C_6H_{12}O_6$).

Although the starch micelles pass through filter-paper, they are long and entangled. They show colloidal properties and a marked degree of thixotropy. (The viscosity of the solution increases when left in rest and diminishes with intense stirring).

Our own explanation was based on the orientation of the starch molecule entering into the field existing near the surface of a clay particle surrounded by swarming H⁺ cations, fig. 6, 7 and 8. The OH⁻ ions being repulsed to the further end and the resulting displacement of the opposite ions, swarming round the points give rise to an electric field of such intensity that the OH⁻ ions either leave the points or the chain of starch links disrupts.

¹⁾ Leerboek der Organische Chemie, p. 331 (1932).

²⁾ Leerboek der Organische Chemie, p. 304 (1932).

An observation of Prof. KRUYT during the verbal discussion of my communication and the very recent publication of the remarks of Dr. J. H. DE BOER at the symposium on hydrophobic colloids at Utrecht induce me to give full credit to DE BOER's explanation, which is as follows:

In the kaolin-suspension, as well as in the starch solution we are dealing with negatively charged particles, so that the explanation of the flocculation

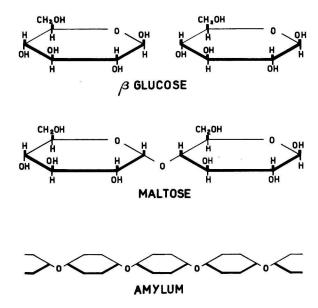


Fig. 5. Formula of amylum in relation to those of maltose and glucose, showing its chainlike structure of indefinite length.

phenomena, described above, cannot be sought in a mutual flocculation of two colloids with opposite sign of charge. Apparently we are dealing with the phenomenon of "sensitization" of a hydrophobic suspension with a small amount of a hydrophilic colloid, the particles of which have a similar

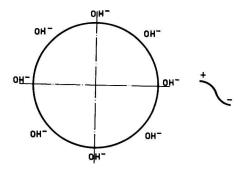


Fig. 6. The coal- or clay-particle has a negative charge by the adsorbtion of OH—ions. It induces a separation of electricity on a starch molecule hovering in its proximity.

sign of charge as the particles of the suspension. This subject has been treated during the symposium on hydrophobic colloids in Utrecht on the 5th and 6th of November 1937 by Mr. Overbeek 1). In his lecture, after giving several examples of sensitization and treating different explanations given in litterature, Mr. Overbeek reaches to an explanation, which in its main points was already suggested by Zsigmondy 2). According to this view the suspensoid particles will tend to envelop the hydrophilic ones and cluster together to coarser particles, a mechanism which decreases the stability of the suspension. Amending this theory Mr. Overbeek assumes

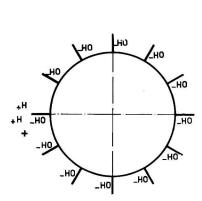


Fig. 7. The starch molecules stick to the surface with one end and remain stiffly erected by the electric repulsion acting on the free end. H^+ ions swarm round these ends.

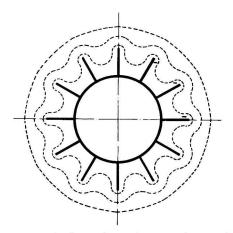


Fig. 8. Surface of equal potential around a sphere provided with spikes.

that after adding the hydrophilic colloid, aggregates are formed consisting of one suspensoid particle and one or more hydrophilic particles, which are every time smaller than the hydrophobic one. We must assume that some ions of the double layer are pushed aside if the hydrophilic particle is attached to the hydrophobic surface. These aggregates will exert an increased mutual attraction force and a decreased mutual repulsion force, so that they will flocculate already at a much lower electrolyte concentration than the original hydrophobic colloid before adding the hydrophilic particles.

In our special case, we might build on some discussion remarks made by DE BOER 3) and assume that the molecules of starch added by us in very minute concentrations will be bound on the surface of the kaolin particles in such a way, that the hydroxylgroups, there are three of them in every

¹⁾ J. TH. G. OVERBEEK, Chem. Weekbl., 35, 117 (1938) and the symposium-book which will be published in due time.

²⁾ R. ZSIGMONDY and E. JOEL, Z. physik. Chem., 113, 299 (1924).

³⁾ J. H. DE BOER, Discussion remark Chem. Weekblad, 35, 122 (1938).

pyronoid ring of 5 carbon atoms and 1 oxygen atom of the starch chain, point with their dipoles towards this surface, the pyronoid rings having a flat position. In that way the hydrophilic character of the starch cannot manifest itself. The kaolin particles provided with such starch molecules in a flat position on their surface will attrack each other with an increased attraction force as the VAN DE WAALS forces starting from the hydrophobic backs of the starch rings will attrack other hydrophobic backs attached to other kaolin particles better than they will attrack water molecules. Sche-

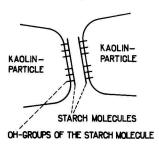


Fig. 9. Sketch of DE BOER, illustrating how kaolin or clay particles show a tendency to stick together, when covered by starch molecules. After loosing their hydrophilic character the backs repulse the water and attrack each other.

matically we might give the following picture of the mechanism described here (fig. 9).

This explanation of DE BOER is attractive as it explains at the same time, why sludge precipitated by starch dewaters easier than when precipitated by electrolytes, and also why the addition of a small amount of starch to coal particles recovered by the froth flotation process facilitates the dewatering on a suction filter.

5. The new Clarification Plant at Statemine Maurits.

In paragraph 3, sub a, it was already mentioned that flocculation by an electrolyte is too expensive and the precipitate too bulky. For these reasons a more modern plant had to be designed and starch had to be adopted as

flocculator. The problem was to deal with water containing about 17 grams of solid matter per litre, composed of some dispersed coal but chiefly of tailings (clay) from the froth flotation plant, ash and fluedust from the steam boilers collected by Modave-catchers.

Per minute 20 m³ of effluent with 333 kg of solid matter has to be treated amounting to 10 millions m³ with 167000 tons of solids yearly.

For several years extensive research on flocculation was carried out in the central laboratory of the State Mines by Dr. H. PIETERS and his staff. It is impossible to give an abstract of the results that would do justice to their work. Full scale experiments were made at State Mine Maurits with a Baum-cone by Ir. H. MEYER with the object of finding the way of operating, that would give the least expenditure on chemicals and of trying the effect of baffles.

The prices of flocculating agents are subject to considerable fluctuations. On the next page we give the figures of some time ago. Only the proportion of the costs of the different systems is to be considered.

Statemine Maurits.

Clarification of washery-, boilerhouse and mineffluent with 16,7 grams of solid matter per litre.

Flocculator	Amounts needed grams/litre	Costs p. m ³ (dutch cents)
Lime	0.76	0.65
Potato starch	0.11	0.60
Ferrous sulphate	0.185	0.36
Mixtures of ferrous sulphate	0.100	0.192
Potato starch	0.050	0. 27 5
	Total costs 0.467	
First potato starch and in a second stage	0.030	0.165
Ferrous sulphate	0.012	0.023
	To	otal costs 0.188

FLOW SHEET OF CLARIFICATION PLANT STATE MINE MAURITS

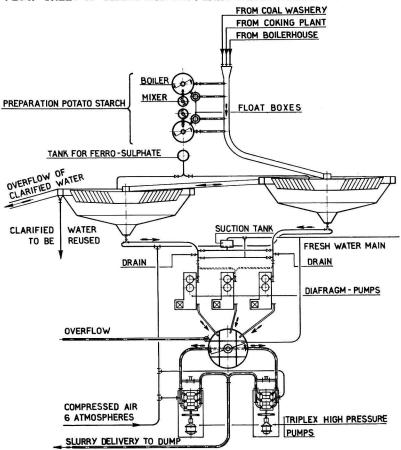


Fig. 10. Flow sheet of new clarification plant at Statemine Maurits.

Quantities and costs of flocculators.

It will be clear that the savings obtained bij the last mentioned procedure induced the State Mines to adopt clarification in two stages for the new clarification plant at Statemine Maurits.

For that purpose two thickeners in series had to be installed and the expenditure on flocculators amounts to 20.000 guilders a year. The other costs of operation are also high, but this sacrifice is considered to be justified for getting a clear effluent.

The plant is represented schematically in figure 14 and a more detailed drawing of the thickeners is given in figure 15. Special attention is drawn to the baffles placed above the scrapers, because these are generally omitted, although a profuse literature shows their utility 1).

The slurry or flocculated sludge is pumped by triplexplunger pumps to the top of the refuse heap of the mine about 100 m high and fills the free spaces.

20 METER LIFT I METER

THICKENER FOR FLOCCULATED SLURRY

Fig. 11. Thickener for flocculated slurry showing the arrangement of baffles.

DISCHARGE

Potato-flour and -starch are national products of which some 150.000 tons with a value of tens of millions of guilders per year are exported,

¹⁾ See Handbook of Ore Dressing by A. F. TAGGART, p. 984 (1927). Effect on slime settlement, and all the literature on this subject cited by TAGGART.

The Industrial Chemist, p. 320 (1931). Die Chemische Fabrik, S. 46 (1932).

Report of Fuel Research Board for the year ended 31st March 1931, p. 56. In a tube 2 inches in diameter and 22 ft long placed at 60° to the vertical and in using a slurry containing 30 percent of solid matter the water separated at 70 times the rate observed in a similar tube placed vertically.

Report 1932, Report 1933, p. 52-56, Report 1934, p. 46.

Die Klärung des Schlammwassers aus Kohlenwäschen von W. PETERSEN und F. GREGOR, Glückauf, 68, 621 (1932).

Verbesserung der Schlammwasserklärung durch Schrägstellung der Klärzylinder, von G. LOHMANN. Diss. Techn. Hochschule, Aachen (1935), Glückauf, 72, 1121 (1936). Zeitschr. d. Ver. d. Ing., 81, 941 (1937).

while much more of it is used in the Netherlands themselves. We consider it of interest to draw the attention to this new and promising field of application.

Dr. H. PIETERS and Ir. O. VAN DE LOO obliged me by looking over the manuscript.

Heerlen, 20 January 1938.

SOME OF THE LITERATURE CONSULTED.

- The Clarification of Polluted Water with particular Reference to Colliery Waste and Sewage, by R. D. GIFFORD. The Junior Institution of Engineers Journal, 44, 477—493 (1934).
- Recipe of Mr. IDRIS JONES, Research Manager, Powell Duffryn Associated Collieries.

 Ystrad Mynach Hengoed Glam. 20 parts of potato-flour heated with 5 parts of CaCl₂ and 3 parts of ZnCl₂ and made to a soluble gel.
- American patent 405.038 Alcaline solution of starch submitted to the action of electric current in order that some oxydation occurs by oxygen in status nascendi.
- Invention State Mines: Wet starch with CS₂, dissolved in NaOH, diluted with hot water.

 Never forget that a surplus of starch peptises the dispersion and that it is only economical to dose the starch far below the optimum of flocculating power.
- Dr. Ing. IMHOFF, Essen, writes in: Die chemische Abwasserklärung in Amerika, S. 119:

 "Kalk wird nicht mehr als Fällungsmittel sondern nur als Mittel zur Berichtigung des Säuregrads betrachtet."

 The State Mines however, investigating whether it was necessary to get the pH down to the iso-electric point for starch, found that although the flocculating power of the starch is improved, the application of lime in order to regulate the pH is in most cases too expensive.
- Moderne Afvalwaterzuivering, JAN SMIT, Chemisch Weekblad, 34, 20 Februari, 1937, p. 139—146.
- Treatment of Washery Water. Practical Aspects of Flocculation. Needham. Transactions of the Inst. of Mining Engineers, Vol. XCII, Part 1, 28-58 (1936).
- Flocculation. Its Application to Industrial Problems by J. O. SAMUEL, Chief Research Chemist Emlyn Anthracite Colliery Ltd. Western Mail & South Wales News Eng. Supplement Nov. 20, 1935, p. 17.
- Flocculation in Theory and Practice. Colliery Engineering, Vol. 13, No. 144, 45 (1936). Treatment of Coal Slurry. Iron and Coal Trades Review, Aug. 16 (1935).
- The Conditioning of Washery Water Transactions Inst. Mining Engineers, Dec. (1934). Die Klärung und Entwässerung feinkörniger Aufbereitungserzeugnisse. W. PETERSEN, Metall und Erz, 34, 49 (1937).
- "Sensitisation" and other Observations on Slurry Flocculation by WILKINS. Journal of the Society of Chemical Industry Transactions and Communications, Nov. 29, 1935, p. 392 T.
- Some Aspects of Flocculation. SAMUEL M.Sc. Journal of the Society of Chemical Industry, Aug. 28, 1936, Vol. LV, No. 35, p. 669—680.
- The Clarification of Washery Water and the Recovery of Coal Slurry, LEWIS B.A. The Colliery Guardian, Nov. 15, 1935, p. 895.
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