On rust precipitates present in drainage pipes and on the means of preventing their formation

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In several cases where the deep drainage does not function properly, it has been found that precipitates dyed yellowish-brown by iron compounds have been formed in drainage pipes, seriously diminishing the flow of water and in some cases even causing complete blockage. The flow capacity of pipe joints may also deteriorate directly as a result of precipitates accumulating at the seams. The effectiveness of drainage thus tends to decline continuously. Blockage of deep drainage pipes is common in Finland too, where precipitates are found, not only in fine-sand and sand soils, but particularly in postglacial clay soils and peat soils. Scientific research into the origin of precipitates and into methods for the prevention of their formation has been carried out e.g. in Germany, Denmark and Sweden, but the methods recommended to date for their removal have proved so ineffective that we have considered it advisable to endeavour to throw light on this phenomenon. It is a phenomenon of increasing importance in our country as well, with deep drainage becoming more and more general. A method both effective enough and economically serviceable must be found to counteract it.

Rust precipitation and deep drainage

The influence of the so-called rust precipitates obstructing the working of deep drainage is known wherever migrating iron is present in the soil of cultivated lands (Engelhardt 1949, Feilberg, Aa. & Feilberg, C. L. 1921, Jensen 1938, Langisch 1930, Schledermann—Larsen 1949/50 and Wiklander 1945). The precipitates obviously do

not consist of iron compounds alone, but generally contain, even by ocular estimates, in mineral soil drainage clay and silt elements and in peat soil drainage fine-grained peat. Rust precipitation seems most frequently to occur when draining certain peat soils in the process of being reclaimed, into which surface and soil waters continue to flow from the surrounding iron-containing mineral soils. The risk of precipitation can often be detected almost immediately after they are dug, from the abundant yellowish brown precipitate that appears on the bottom of trap ditches. After the deep drainage of such peat soils, rust precipitate is first formed in silt wells, the water flowing through them being in direct contact with air, and in the discharge drain at the point of entry of the deep drainage outlet.

Should real rust blocks form in the drains or such quantities of precipitate settle there that the operation of the drains is unfavourably affected, the drains must be cleaned. Drains requiring cleaning are readily observed in the spring by the delayed drying up of the area above it. To remove rust precipitate from the piping system, the drain pipe must be dug out at 30—40 metre intervals and opened, the precipitates loosened by means of a lath or wire strip cleaner, and flushed by water through the outlet. It is often necessary to use a firepump for flushing.

Experience has shown that formations of "rust precipitates" generally diminish annually.

No detailed information has been published in literature regarding the nature of rust precipitates. They have simply been defined as iron-containing and gelatinous precipitates. According to observations by men of practice, some of the precipitates are "rag-like" while others do not posses that tough, binding quality to the same extent.

The present investigation was carried out in the commune of Utajärvi, province of Oulu, on a peat soil being cleared for cultivation, belonging to Kolehmainen Farm. The ash content of the dry matter in the rust samples taken in connection with the investigation varies considerably, even with control drains (table 3). This may be due to the fact that the dry matter was obtained by emptying the test drain pipe throughout its length; hence, the dry matter includes both the precipitate proper and any possible silt. The same table also shows that sesquioxides constitute the main part of the ash. The Al₂O₃-determinations taken of two control drains (AARNIO 1915; CORNEY & SCHOLLENBERGER 1928) show that aluminium was present in a considerably smaller quantity than iron, and hence iron was really the most important component in the ash in these cases.

Like iron and aluminium, silicic acid is also present in the soil in colloidal form, forming gels. In addition to these, attention must also be paid to the amount of humus when studying the precipitates in drains. In the samples examined (table 3), silicic acid has constituted the most important component, after iron, in the ash. Compared with iron, aluminium and silicic acid, the other mineral substances have constituted a very small part only of the ash of the precipitates. Moreover, the amount of dry matter in the precipitates in question is fairly small. In the form of gels in natural condition and due to their fairly high water content, they may, however, be large in volume and hence prevent the free flow of water.

The samples examined have contained in declining order of importance humus, iron, silicic acid and aluminium (table 3). It is to be noted, as mentioned above, that any possible silt that does not belong to the precipitates proper, but is included in the dry matter, increases the relative proportion of humus, as the experiment was carried out on a peat soil. Hence, the results do not indicate the humus content of precipitates proper.

Humus is very active but being difficult of solution it is not capable of migrating except in the form of colloidal complexes or humates. Arriving from almost anaerobic surroundings in the drain pipe, such compounds may oxidize to some extent or the colloidal complexes may change their composition, whereas changed conditions bring no considerable alteration in the solubility of humus. Hence it might be expected that insofar as humus enters the drain pipe with water, it is likely to migrate further in it without forming any major obstructions to the flow of water.

When studying the activity of iron in the conditions in question, a distinction must be made between, on one hand, bivalent and trivalent iron, and on the other hand, iron bound to inorganic and organic compounds. Iron migrates in trivalent and simultaneously in inorganic form only in soils so acid that they are incapable of cultivation (Turner 1931; Wiklander & al. 1950). In the ordinary reaction conditions of our fields under plough it migrates primarily in bivalent form. (Halvorson 1931; Ignatieff 1941.) When such dissociated iron enters a drain and comes into contact with air, it is oxidized — either microbially or purely chemically — and precipitates as ferric hydroxide, its pH simultaneously declining slightly. The mobility of the resulting sol depends on the reaction conditions prevailing. With pH increasing, the sol changes into gel, becoming increasingly slow of motion, and coagulates completely in neutral conditions (Mattson 1930). Provided

the drain contains active humus or silicic acid, the precipitated ferric hydroxide will form with them a colloidal complex, the composition of which complies with prevailing reaction conditions (Mattson 1930). The higher the pH, the more iron is bound to the complex, and vice versa.

Iron may also migrate into the drain bound to organic compounds or silicic acid, in ferrous or ferric form. While bound to a colloidal complex, the reaction conditions prevailing in the drain may change its mobility. If the complex migrates into the drain in the form of either an anionic or cationic colloidal complex, and if the reaction of the water flowing in the drain is closer to the isoelectric point of the complex than that of the soil outside the pipe, the complex is precipitated, the precipitation being more complete the closer the pH of the water in the pipe to the isoelectric point of the complex (MATTSON 1931). If again the above reactions differ greatly from one another, the complex, compared with the solution, receives an increasing either negative or positive charge and hence acquires increased mobility. If the flow of water in the pipe is slow the complex may have time, before emerging from the drainage system, to undergo a change in composition and to precipitate isoelectrically. If the new isoelectric point is below the former, the relative proportion of sesquioxides is reduced; in the opposite case it is increased. Ferrous and ferric iron react in these cases approximately in the same way, except that ferrous iron may be oxidized into ferric and that, due to the higher isoelectric point of ferrous humates, the ferrous complexes require a higher pH in order to form cationic complexes. In accordance with the above, it is obvious that the degree of dispersion of the iron-containing colloidal complexes in a drain depends on the reaction conditions prevailing both in the drain pipes and in the soil surrounding them.

In the above, the precipitation of iron in drains was discussed from the chemical point of view. Generally, however, all the investigators dealing with the origin of the precipitates in question have unanimously ascribed it mainly to microbes (Langisch 1930; Jensen & Jakobsen 1946 and Jensen 1938), and considered chemical precipitation quantitatively insignificant (Wiklander & al. 1950). When seeping into the drain pipe, and apparently in most cases even while in the pipe itself, the soil solution comes into a very close contact with the oxygen of the air; hence, the ferrous ions bound to the ionized compounds may oxidize as follows:

$$4 \text{ Fe}^{..} + O_2 + 2H^{.} = 4 \text{ Fe}^{..} + 2 \text{ OH}',$$

from which is obtained, according to the law of mass action,

$$\frac{AFe^{\cdot\cdot\cdot 4}\cdot AO_{2}\cdot AH^{\cdot 2}}{AFe^{\cdot\cdot\cdot 4}\cdot AOH^{\prime 2}}=K.$$

where A denotes the activities of the relevant ions.

The equilibrium equation shows that with oxygen pressure remaining constant and pH decreasing, bivalent iron is oxidized into trivalent. In the pH range in question in drain pipes, the ferric ion does not remain in solution but is oxidized in the form of ferric hydroxide. If the pH were fairly high and no oxidization were to occur, then bivalent iron would precipitate more completely in the form of ferrous hydroxide the higher the pH.

Bound to organic compounds, iron may remain in solution even in conditions where, if inorganic, it would precipitate. This is due to the slight ionization of organic compounds. The precipitation of iron bound to these compounds results from the decomposition of organic radicals, in consequence of which the amount of ionized iron grows beyond the solubility limit. The decomposition of organic radicals, again, is due to microbial action; hence, the microbes in this case indirectly precipitate iron (Starkey & Halvorson 1927).

Generally it can be said that the precipitation of iron in nature is determined by the pressure of oxygen and carbon dioxide and by the hydrogen ion concentration of the solution. Bacterial action has generally been found in connection with the precipitation of iron, but this can hardly suffice, however, to prove that iron does not precipitate purely chemically and wherever conditions are favourable for chemical precipitation. This again does not exclude the possibility that the oxidization and precipitation of iron by bacterial action might not advance further than they would by purely chemical processes.

Hence, iron enters drain pipes ionized, but is precipitated there in the form of ferric hydroxide. The origin of ferric hydroxide still does not presuppose its precipitation as, being a colloidal sol, it may remain in solution. Positively charged it is, however, capable of absorbing negative ions from the solution, and precipitates after shedding its charge. Ferric hydroxide is hardly capable of staying in sol condition in a drainage pipe but precipitates due to the action of anions or humus (AARNIO 1915).

In colloidal complexes the silicic acid has the same qualities as humus. In drain precipitates, silicic acid does not really take any part in reactions but nevertheless affects the properties of colloids quite considerably.

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When studying the importance of the different components in drain precipitates it is to be noted, therefore, that iron migrates to the drain pipe either completely ionized or at least ionized to some degree, and generally precipitates there. Precipitation in itself does not always adversely affect the flow of water in the piping, for in the majority of cases the resultant amount of ferric hydroxide is so slight that it is flushed away by water from the drain system. It is to be noted that ferric hydroxide, being a lyophilic colloid, does not increase to any great extent the viscosity of the mother liquid. Silicic acid, on the other hand, which is a lyophilic colloid, increases the viscosity of the mother liquid and makes it more slow-moving. In this respect, therefore, it may have a considerable importance in the colloid complexes in question. Similarly to silicic acid, humus acids also are gels containing a great deal of water. Through electrolyte action they coagulate, and their ability to bind water is reduced at the same time. Due to great internal friction, humus acids also, like silicic acid, increase the viscosity of the mother liquid. The viscosity of the precipitates in question is obviously also affected by the force of the electric charges of humus-containing colloidal complexes. The greater the electric charge of the particles, the more fine-grained is the sol they form.

Iron bacteria also can probably be assumed to affect the physical qualities of the gel surrounding them, expressly the viscosity, by forming a kind of reinforcing network in the gel in question. For instance, Dorf (1932) found, when studying a drain precipitate, that Gallionella and a close relation of this bacterium, Spirophyllum, had formed an innumerable quantity of fine threads in the gelatinous mass.

Countering rust precipitates

Method based on the toxic effect of copper

In countering the iron-containing precipitates originating in drain pipes, an attempt can be made either to prevent the occurrence of the precipitate in the drain pipe itself, or to prevent precipitate-forming substances from gaining access to it. If the first alternative is chosen, it must further be decided whether the counter-measures are to be directed against iron precipitation by chemical or biological processes. In the investigations reported in the literature to date (Langisch 1930; Jensen 1938 and Jensen & Jakobsen 1946), the latter alternative has been chosen, as it was assumed that iron was precipitated in drain

pipes as a result of bacterial action. Hence it was concluded that if bacteria can be destroyed, iron precipitation will also be inhibited. Copper has been used, in every one of these experiments, for the destruction of bacteria. The use of copper in this connection is based on the observation made by Wilhelm von Nägel, of Switzerland. that even very small amounts of copper and silver have a strongly bactericidal effect in water. (Wiklander & al. 1950.) Therefore, if water flowing in drain pipes were in contact with e.g. copper, bacteria would have no chance of living in it. To investigate the influence of copper in practice, Langisch (1950), of Germany, arranged the following experiment. A copper lining of approx. 80 mm in width was placed in the joints of drain piping. Water suitable for the purpose was then allowed to enter the pipes and was recovered. The water proved to be distinctly copper-containing, and remained clear even when stored for a long time. On the other hand, when water was allowed to enter pipes through a seam not lined with copper, Leptothrix ochracca colonies developed in the water after some time. Continued experiments by Langisch in fact proved that copper was a reliable poison for the destruction of the said bacteria.

Jensen (1938) again studied, in a laboratory experiment, the influence of copper on the activities of bacteria oxidizing bivalent iron. He reduced water taken from a drain and containing iron precipitate until the brown colour of the ferric hydroxide was no longer discernible, divided up the sediment into two bottles, in one of which he placed metallic copper, and passed a current of air through the water in the bottles. The water in the bottle into which no copper had been added quite soon turned reddish in colour, indicating that bivalent iron had been oxidized into trivalent iron, whereas in the bottle with copper added the colour of the water remained unchanged, the copper evidently destroying the bacteria precipitating iron.

Attempts to prevent the formation of iron precipitates in drain pipes with the use of copper have been based on the bactericidal effect of copper. However, used in this way, copper may affect the equilibrium of iron purely chemically as well.

A semi-precious metal, copper does not actually dissolve in other than oxidizing acids, but in the presence of air it slowly dissolves in other acids as well, and even in weak organic acids:

$$2 \text{ Cu} + \text{O}_2 + 4 \text{ H} \cdot = 2 \text{ Cu} \cdot \cdot + 2 \text{ H}_2\text{O}$$

Hence, it is obvious that, in the experiments by Langisch reported above copper has been dissolved to some extent, as atmospheric

oxygen is generally available in drain pipes, and soil solution usually contains weak organic acids.

To study the influence of copper on iron solution, let us observe the cell reaction:

The basic electromotive force obtained for the cell is 0.431 v, which means that copper reduces trivalent iron practically entirely to bivalent iron. To observe the phenomenon, the following experiment was arranged. 0.01 M ferric chloride solution was placed in two flasks, and a copper plate inserted into one of them. Changes in the electromotive force and hydrogen ion concentration in the two solutions were then observed. The same experiment was carried out using 0.01 M ferrous chloride and water taken from a drain pipe and containing iron precipitate. This water had been stored in a bottle for about a year, and hence ferric iron had been reduced fairly completely to bivalent form, as no ferric hydroxide reddish colour was discernible in the water. Results of the experiment are given in table 1.

The ferric and ferrous chloride solutions with no copper remained clear to start with, however gradually acquiring, due to hydrolysis, the yellowish colour resulting from ferric hydroxide. For the same reason the electromotive power of ferric chloride declined slightly and the pH increased. With ferrous chloride again, obvious oxidization occurred. The ferric chloride to which copper was added, reduced very strongly and rapidly in accordance with the above, and in such a way that both solutions with copper added finished in the same state of equilibrium, as was to be expected.

It was surprising in the experiment to note the fairly intense and

 $Table \ 1.$ Influence of copper on the electromotive force and hydrogen ion concentration of iron chloride solutions.

Duration of	FeCl ₃		FeCl ₃ + Cu		FeCl ₂		$FeCl_2 + Cu$		m e H		Drain pipe water + copper	
Experiment	e mv	рН	e mv	pН	e mv	pН	e mv	рН	e mv	рН	e mv	рН
beginning	848	1.10	848	1.10	400		400			5.91		5.91
24 hours				3.91			459					
7 days							465					
14 days	802	1.62	462	4.60	420	3.99	457	4.70	452	5.19	416	5.68

rapid formation of ferric hydroxide that occurred in both the solutions to which copper was added. It became rapidly visible in colour and later even as precipitates. The result was the more surprising as no indications were found in the literature which might have assisted in the interpretation of the phenomenon in question; on the contrary, JENSEN'S (1938) experiment yielded an entirely opposite result. However, as copper reduces trivalent iron to bivalent iron, it must possess a fairly strong ability to precipitate ferric hydroxide, as it is capable of bringing about precipitation of fairly small ferric hydroxide concentrations. The phenomenon would be understandable if copper could be explained as capable of neutralizing the positive charge of ferric hydroxide sol. Copper, a positively charged ion, one would expect, however, on the contrary to promote the rentention of ferric hydroxide in solution. However, due to the complex-forming property of copper ion, it may change into being negatively charged. Copper hydrate ion, Cu (H2O)4., which binds 4 water molecules, tends to exchange water molecules for chloride ions, forming the chloride compound series:

BUST PRECIPITATES PRESENT IN DRAINAGE PIPES

$$Cu(H_2O)_4$$
, $CuCl(H_2O)_3$, $CuCl_2(H_2O)_2$, $CuCl_3(H_2O)'$, $CuCl_4''$.

Negative complexes are formed to any considerable extent only in the presence of chloride ion surplus.

In the experiment reported above what occurred is obviously that these negative chloride complexes of copper were formed which, being negative ions, were capable of precipitating positive ferric hydroxide colloids. Examination of the samples taken showed that in the water in question iron is strongly reduced. However, due to the action of atmospheric oxygen, it was gradually oxidized during the experiment, with the pH dropping at the same time. To start with copper accelerated oxidization, but later on retarded it. The amount of iron present in the solution was not determined, but copper in this case too had an iron-oxidizing effect, as the pH at the conclusion of the experiment was as high as 5.68, the corresponding figure without copper being 5.19. The course of the reaction, therefore, was exactly the same as in the experiment carried out with ferrous chloride. From this the conclusion can be drawn that copper hydrate ion is capable of forming negative complexes with organic anions as well. (This because drain pipe water could not contain mineral acids — in the first place sulphuric acid — as the pH of reduced sediment was slightly on the acid side, and the pH, as a result of oxidization and hydrolysis, did not decline to any extent worth mentioning.) Hence, use of copper would

promote and not reduce precipitation of iron in drain pipes, in spite of its being capable of destroying the bacteria, as had been conclusively shown, in the experiments by LANGISCH (1930).

To what extent copper hydrate is capable of forming the above mentioned complexes with the anions present in the soil solution has not been investigated in detail. However, it might be expected that the formation of negative complexes would advance with the concentration of organic acids growing. When the anion concentration of soil solution is low copper hydrate would form with the anions of the solution apparently uncharged or positive complexes only, which would merely promote retention of the ferric hydroxide sol in solution. In practice this would mean that with soils rich in humus the use of copper in drain pipes would promote the formation of iron precipitates, whereas with mineral soils poor in humus it might decrease it by reducing trivalent iron to bivalent iron.

JENSEN'S laboratory experiment reported above, in which copper had prevented the precipitation of iron, which the author assumed to be due to the destruction of bacteria, could, from the above, be interpreted as indicating that the copper had reduced the trivalent iron to bivalent iron, and thus prevented its precipitation in the form of ferric hydroxide. And further, due to either too low anion concentration or the type of anions, the copper had been incapable of forming with them negative complexes which could have precipitated the ferric hydroxide sol always present in a slight amount.

JENSEN (1946) investigated also the effect of copper in countering precipitates by *field experiments*. Copper was used in the various test members in the following ways:

- 1) A copper strip, 20 mm wide and 0.15 mm thick, was placed in the drain pipe.
- 2) Pipes were used the exterior surface of which had been treated with copper.
- 3) Both ends of the pipes were buried, previous to burning, in a mixture of clay and copper powder.
- 4) The pipes, prior to burning, were buried in mixture of clay and copper sulphate. After burning, the copper present on the interior and exterior surfaces of the pipes was reduced to metallic copper.
- 5) A cylindrical copper plate, 0.15 mm thick, was placed in each pipe, throughout the length of the pipe.

After the pipes had been in the earth for 5—7 years, a check of the drains was effected, and the precipitates assembled in the pipes were

Table 2.

Results of Jensen's field experiments.

Exp.	К1	K2	КЗ	К4	K5	Cu1	Cu2	Cu3	Cu4	Cu5	Cu6	Cu7	Cu8	Cu9
1 2 3 4 5	1.4 0.06 1.3 0.45 0.23	5.3				0.21 10.5	6.6 0.78	0.30 0.94 3.1 2.3 1.18	4.0	2.02	0.12	0.67	0.08	2.35

Table 2 (cont.).

Evn	Mean value						
Exp.	К	Cu					
	Ä						
1	1.13	5.13					
2	0.07	0.75					
3	3.3	6.05					
4	0.78	1.76					
5	0.55	0.88					

taken and subjected to a quantitative analysis. Table 2 gives a short summary of the results of this experiment. K indicates control test members without copper and Cu those with copper. The results are given in grams of ferric oxide (Fe₂O₃ · 3 H₂O) per pipe.

The author himself mentions that the experiments give a result that is neither positive nor negative regarding the effect of copper. Schledermann—Larsen (1949/50), who subsequently described the experiment, mentions that it seems as if copper had promoted the precipitation of iron. From a study of the results it does seem evident that the copper has promoted the precipitation of iron in all the experiments, and even fairly strongly. If it is assumed that the copper had destroyed the bacteria, the experiment would prove that iron had oxidized chemically and that the use of copper had promoted its precipitation in compliance with the theoretical explanation offered above.

Countering rust precipitates by chemical methods

As another alternative to the bactericidal method, efforts could be made to prevent by chemical methods the precipitation of iron that has migrated into the drain pipes and to reduce the ferric hydroxide

present there to bivalent form, thus reconverting it to a mobile form. This would involve, in the first place, the raising of the surface of soil water above the pipes. As a result, oxidization would be prevented in the absence of air, and due to reducing conditions ferric hydroxide might partly be reduced back to ferrous form. For instance in the laboratory experiments carried out by IGNATIEFF (1941), the reduction of ferric iron, in conditions of the nature described above, first occurred slowly, but was fairly remarkable within 2—3 days. According to the author, the reduction was mainly a biological process. The intensity of the reduction would depend on the extent to which ferric hydroxide, as it grew older, would have had time to change into irreversible form.

To favour the above reduction processes and to prevent oxidization in drainage pipes, a system of so-called underwater drainage has been evolved in Finland in some cases, so that the drain network in its entirety, including its outfall, has been kept continuously submerged by means of dams in the ditches. Drainage then works according to the principle of "connection vessels", and drainage depth is determined by the height of damming. Because of gradients this possibility seldom exists, but at least in cases where the method has been successfully employed no direct drain blockages have occurred from rust precipitation. Freckman (1931) also refers to the use of submersion, but considers it fruitless as the formation of rust precipitates, according to him, is a biological occurrence.

Apart from preventing the precipitation of iron in the drain pipe itself, another main alternative would be to halt the migration of iron by causing it to precipitate before it reaches the pipe. In practice this would best be carried out making conditions in the immediate vicinity of the pipe favourable for the precipitation of iron.

Iron precipitates, as described above, are primarily due to the high pressure of oxygen and a high pH. High oxygen pressure promotes the oxidization of bivalent to trivalent iron, which again is precipitated in the form of hydroxide at a lower pH and in bivalent form. A high pH, again, in itself promotes the precipitation of iron in hydroxide form.

Iron precipitation reactions based on high oxygen pressure could be utilised in countering drain pipe precipitates by filling the ditch, once the pipes are laid, with as coarse-grained soil as possible. This would result in the desired increased aeration of drain packing and higher oxygen pressure compared with the surrounding soil.

One counter measure of this nature is employed in Finland, in

districts where formation of rust precipitates is probable, viz. to dig drains initially to half the depth only, and then leave them temporarily to operate as open ditches. Provided the area is also limed intensely, abundant leaching of anionic colloidal complexes can be expected due to the sudden rise of pH above the isoelectric point of the complexes and to the fact that ferric hydroxide would still not have had time to assume irreversible form as a result of drainage activities. Later on, often not until the following year, when the ditches are dug deeper, the precipitate is removed, and it is often found that a great deal of it has been formed on the bottom of the ditches. Experience has shown that this procedure considerably reduces the subsequent risk of drain blockages and, due to the drying up and sinking of peat soil, facilitates work on drainage. In Denmark they plan to continue experiments along the lines of Hedeselskabet, by covering drain pipes with a layer of small-stone gravel, lime stones and copper compounds (Schleder-MANN-LARSEN 1949/50). The results of these experiments have so far not been published in literature.

To what extent a high pH promotes the precipitation of iron depends primarily on the form of iron migration. It can perhaps be assumed that in approximately neutral reactions ionized iron is precipitated in almost its entirety, while weakly ionized iron, bound to organic compounds, is apparently capable of passing through even such a pH level. In addition, the reaction of the surface soil is of importance here, insofar as the more acid it is, the lower is the iron content of the complexes originating in it, and the larger the negative charge which they possess (i. e. at a higher pH), the more they are retained in solution. This type of situation may be assumed to arise when fields are limed, as shown e.g. by a liming experiment carried out by Keso (1940). Mann (1930) has also observed the same phenomenon. If, on the contrary, the reaction of the field should decline rapidly for some reason, iron-containing complexes, positively charged, would start moving and be precipitated on reaching a region of higher pH level.

A laboratory experiment was arranged in order to clarify the extent to which ionized bivalent iron is precipitated in anaerobic and approximately neutral conditions. At the bottom of a glass cylinder some 30 cm in height an approx. 5 cm thick layer of humified Sphagnum-Carex peat was placed, topped by a thin layer of limestone powder; the cylinder was then filled with peat. Diluted ferrous chloride solution was poured into the cylinder. On passing through the peat and the lime layer the solution flowed out from an opening at the

bottom of the cylinder. Solution was added to the cylinder in small quantities, so that the fluid level in the cylinder was not allowed to sink much and anaerobic conditions were maintained throughout in the soil. The experiment was carried out with varying amounts of limestone powder, and also with different quantities of burnt lime. The experiment showed that the burnt lime had precipitated the iron so completely that the solution which passed through, qualitatively tested, no longer gave an iron reaction, whereas the layer of limestone powder had let through so much iron that the solution gave an easily recognizable iron reaction. The slower the passage of the solution through the soil, the more completely was the iron precipitated. The different lime quantities used, by contrast, seemed to have no significance other than that the neutralisation capacity of the larger quantities was higher. The more effective iron precipitation capacity of burnt lime is naturally due to its greater and more rapid solubility and ionization.

A field experiment was also arranged in summer 1949 in addition to the laboratory experiment, on the peat soil mentioned above that was being cleared for cultivation — on Kolehmainen farm of Utajärvi commune in the province of Oulu. The functioning of the drainage carried out in the previous year (some 26 ha) had been greatly restricted by rust precipitation, and a considerable part of the drains had had to be cleaned twice and even three times. Underwater drainage was impracticable due to the gradients of the terrain. Moreover, it was considered that the digging of all drains to half depth only and their completion in the following year would have retarded clearing work too much. Drainage was therefore continued in 1949 in the normal manner, and if necessary the ditches were cleaned from rust precipitates. Simultaneously a field experiment was arranged on an area to be drained where, according to previous experience, abundant formation of rust precipitates was to be expected. Peat in this section was relatively humified (H6) Sphagnum-Carex peat, the reaction of which, according to numerous determinations, was found to vary slightly, but to be generally somewhat over pH 6.

The drainage area in question was drained in its main parts in July 1949, but as early as the same autumn the whole ditch, due to blockages, had had to be cleaned twice. For the purposes of the experiments, suction ditches 1—7 were extended in November 1949, and their upper ends, for a length of 20 metres, were reserved for the present investigation (Fig. 1). Of the experimental ditches, ditches 1, 4 and 7 were completed in the normal way, dropping a layer approx.

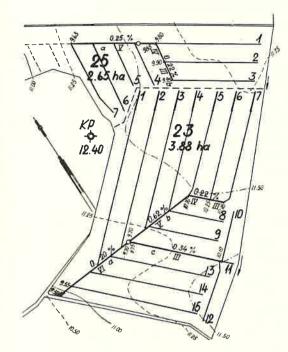


Fig. 1. Drainage system of the experimental field

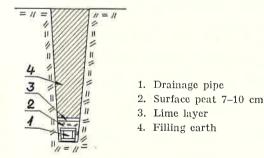


Fig. 2. Profile of drain

7—10 cm in thickness of weakly humified surface peat on the sides and top of the board box used as piping material, and then filling the ditch with the soil removed from it during the excavation. When making experimental ditch 2, a copper wire 4 mm in diameter was drawn along the bottom of the board box. In ditches 3, 5 and 6 limestone powder was used to increase the pH, in quantities of 2.0, 1.0 and 0.5 kg per metre of ditch, spread as evenly as possible on the surface of the weakly humified peat layer on top of the board box. (Fig. 2.)

The experimental ditches were opened at the beginning of July 1950, or some 8 months after their completion. On emptying the board box in each ditch its contents from the entire 20-metre length were carefully preserved for study. In this connection the following ocular observations were made:

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Experimental ditch 1 — control test: the interior surface of the lid of the box was covered with an iron precipitate 1—2 mm thick. At the bottom of the box the precipitate was also relatively abundant, a part of it moving along with water and "rag-like" in appearance. Precipitate retarded the flow of water. Total volume of precipitate and water, 20 litres. Precipitate sank rapidly to the bottom of the vessel.

Experimental ditch 2 — 4 mm copper wire: greyish slime here and there inside the lid of the box. In the box a small amount of light precipitate, moving easily with water. Quantity of water 10 litres. The precipitate sank very slowly to the bottom of the vessel.

Experimental ditch 3-2 kg $CaCo_s/m$: Inside of the lid of the box slightly brownish. The box clean. When emptied, however, it yielded some greyish precipitate. Water quantity 7 litres.

In the filling soil of the opened ditch a thin brown crust was visible on the surface of lime lumps.

Experimental ditch 4—control test: Inside of the lid of the box full of brown rust, thickness of layer approx. 2 mm. Box half-filled with precipitate preventing the flow of water. Precipitate heavy but not "rag-like". Water quantity 15 litres.

Experimental ditch 5—1 kg CaCo₃/m: Inside of the lid of the box completely clean. A small amount of grey or black precipitate in the box. Water quantity 8 litres. Flow of water unobstructed.

Experimental ditch 6 — 0.5 kg CaCO_s/m: Inside of the lid of the box covered by slightly greyish slime. A "rag-like" slime-covered, greyish precipitate was seen in the box, which seemed to obstruct the flow of water to som extent. Water quantity 15 litres.

Experimental ditch 7 — control test: Inside of the lid of the box covered by a grey layer of slime; rust-coloured precipitate along the water opening. The box contained a "rag-like" and gelatinous precipitate floating on the water. No firm precipitate at the bottom of the box, as had been distinctly discernible in the other control tests. Water did not flow in the box. Water quantity 30 litres. (An open ditch 1 m in depth dug several years ago 9 m from the experimental ditch to serve as a trap ditch.)

As can be seen from the report on the experiments, precipitate was

 $Table \ 3.$ Analysis results of drain precipitates.

Ditch	Dry matter	1	s of tion	A	sh	$\Lambda l_2 O_3 +$	$ ext{Fe}_2 ext{O}_3$	SiO ₂	
	g	%	g	0/ /0	g _	% Ash	g	%Ash	g
Co-test 1	56.17	75.1	42.18	24.9	13.99	75.9	10.62	17.8	2.49
Co-test 4	54.52	59.9	32.66	40.1	21.86	86.1	18.82	10.4	2.27
Co-test 7	13.45	81.2	10.92	18.8	2.53	48.6	1.23	36.3	0.92
Cu (2)	27.92	75.5	21.01	24.5	6.84	81.3	5.56	12.2	0.83
0.5 kg CaCO ₃ (6)	21.58	83.4	18.00	16.6	3.58	20.7	0.74	48.5	1.74
1.0 kg CaCO ₃ (5)	16.28	83.2	13.55	16.8	2.74	59.9	1.64	26.9	0.74
2.0 kg CaCO ₃ (3)	44.12	67.5	29.78	32.5	14.34	75.0	10.75	16.0	2.29

present in all control test ditches, in two of them in quite large amounts, but in the third (ditch 7) considerably less. This is probably due, in part at least, to the open ditch in the vicinity of the experimental ditch and to the fact that the water in the box, due to an obstruction further down in the ditch, failed to flow and the box filled with stagnant water.

Among the limed ditches precipitate was present in the ditch that received the smallest amount of lime, whereas the other two were fairly clean. According to ocular estimates the use of lime, therefore, seems to reduce the formation of precipitate.

The samples taken from the boxes at the opening of the ditches were dried and examined in the laboratory. (Table 3.)

Analysis of the results shows that they are not consistent with the observations made in the field. The third control test ditch in particular differs considerably from the other control tests, apparently just because of the above mentioned open ditch and the flooding of the pipe with water. The difference between the observations made in the field and the results achieved in the laboratory is greatest with test ditch 3 (2 kg CaCO₃). Ocularly examined, there was hardly any precipitate present in the drain pipe, but the analytical result shows that it contained a relatively large quantity of iron. An evident contradiction obtains here between the amount of iron and the precipitate. Taking into consideration both observations made in the field and the analytical results, it can be said that the general tendency shows the use of limestone powder distinctly reduced the precipitation of iron within the drains. The influence of copper also seems, in this experiment to have been similar.

 $Table \ \ 4.$ Viscosity and acidoid-basoid ratio of the precipitates.

Test member	Nature of precipitate	$\frac{\text{SiO}_2 + \text{humus}}{\text{RO}_2}$	$\frac{\mathrm{SiO_2}}{\mathrm{RO_2}}$
Control test (7)	"Rag-like" Light, mobile	26.67 9.63 4.21 3.94 1.86 8.71 2.97	2.35 0.75 0.24 0.15 0.12 0.45 0.21

The part played by silicic acid and humus in increasing the viscosity of the colloidal sol or gel and the significance of viscosity in drain precipitates have already been described above. It is therefore of interest to study whether these conclusions are compatible with practical observations. In the field, in connection with the opening of the ditches, special attention was paid neither to the toughness of the precipitate nor to mention viscosity measurements, but observations on the sliminess and "rag-like" quality of the precipitates, which qualities characterize high viscosity, were noted. Table 4 gives observations on the quality of the precipitates in the descending order of their viscosity. No accurate annotation was available regarding the nature of the two last mentioned precipitates. In addition, the table gives the silica sesquioxide ratio and the silica + humus sesquioxide ratio, which affect the quality of the precipitates in the first place. The higher the ratios, the higher should be the viscosity, or sliminess and "rag-like" quality of the precipitates.

In the absence of accurate viscosity measurements it was necessary to arrange the results in the table somewhat arbitrarily. This can probably be considered, however, with the assistance of explanations, as the obvious viscosity order. The table shows the compatibility with which the acidoid/basoid ratios decrease with reduced viscosity. As the two calculated ratios vary along similar lines, the experiment does not reveal the ratio followed by the viscosity in the first place.

The results obtained would appear to indicate that an investigation of rust precipitates in drains should not concern itself solely with the quantity of iron but of silicic acid and humus as well. Both the quantity of the precipitates and their acidoid/basoid ratio should, therefore, be taken into consideration.

To revert once again to the contradiction that obtained between observations in the field and the analysis of the precipitate from experimental ditch 3 (2 kg CaCO₃/m), the natural explanation is to be found in the above. The iron started migrating in the form of an anionic colloidal complex, the electrical charge of which increased further when the complex arrived at a level where the pH was raised by liming. The lime precipitated the ionized iron but promoted the mobility of iron bound to complexes. Hence, the optimal situation, it could be concluded, is one in which ionized iron is precipitated practically completely, prior to its arrival in the subsoil drain, but in which conditions nevertheless favour as little as possible the mobility of iron bound to complexes. Such conditions are apparently associated with a pH of 6. This would explain, in part at least, the fact that in the field test, smaller applications of lime reduced the amount of iron present in the pipe. On the other hand it is to be noted that although with an increased amount of lime the amount of iron present in the drain pipe is increased, the iron has precipitated so strongly into anionic complexes that it is incapable of forming precipitates in the drain and is flushed out of the drain system by water. A good example of this is experiment ditch 3 (2 kg CaCO₃/m). In addition, it must also be borne in mind, that the effective period of small application of lime may be too short in duration.

The experimental ditch with copper wire 4 mm in diameter (Aschan 1907) contained a fairly large quantity of iron but, obviously due to the low acidoid/basoid ratio, the precipitate was light and mobile.

In 1950, when land clearing work was continued on the Kolehmainen farm, some 23 000 kg of limestone powder, or approx. 2 kg per metre of drain, were used to protect the deep drainage system of an area of 22.44 ha. A part of the main ditches and a few suction ditches next to the trap ditch had been dug to half-depth the previous year and left to function as open ditches. When these ditches were later dug deeper, relatively large amounts of rust precipitate were found in them. After the completion of drainage in the autumn of 1950 no rust blockages were present in the drains, and in the spring of 1951 the drains in the area in question operated entirely satisfactorily; hence, the use of lime seems to have led to the desired result in this case.

When lime is used in drains the risks must also be considered that may result from precipitation of iron outside the drain pipe.

Old drains on mineral soils have in certain cases been found to work unsatisfactorily, due to the fact that the water flow capacity of the

pipe seams has decreased. This is considered to be partly due to the fact that the pipes, when fitted in position on the wet ditch bottom. became soiled with clay and silt gruel, and that the fine-grained elements, even though the pipe system may subsequently have been protected with a layer of gravel, later accumulated gradually in the joints. In addition to silt elements proper, the migration of iron may also have contributed to the blockage of pipe seams, as is indicated by investigations carried out in Sweden (FLODKVIST & GUSTAFSSON 1938). Hence, when using lime as a safeguard to prevent the formation of rust precipitates, care must be taken, on mineral soils in particular, not to spread the lime too close to the pipe system, where it may promote precipitation at the seams as well. Iron precipitated outside the drain pipe system by the use of lime may also, later, if the pH falls, be redissolved and enter the drains in reducing conditions. This risk, however, is decreased by the fact that the ferric hydroxide gel, as it gets older, changes into an increasingly irreversible form, particularly if exposed to some extent to the action of air. In addition, at this stage, the amount of iron arriving from elsewhere would be so slight that the iron dissolved at a later stage would probably be flushed out of the drain system.

Without discussing the mobility of humus and silicic acid in any greater detail, it may be mentioned that the most favourable conditions for their migration into drains exist when an acid surface soil layer on top of a less acid subsoil is limed. In practice this condition occurs or may occur when a peat soil, on being taken into cultivation, is limed, and the pH of the soil increases in the vertical direction of the profile. This is quite general in peat soils, since the quality of peat usually deteriorates as the peat layer grows in depth. Hence, in cases like this special preparations should be made to counter formation of precipitates, as in such conditions the iron, too, may become mobile.

Summary

The present investigation deals with rust precipitates present in drain pipes which adversely affect the functioning of the drains, and with methods for the prevention of their formation. To start with, the mobility, migration and precipitation of iron has been discussed, and attention paid to the quality of the precipitates, particularly their viscosity, which was assumed to be due to the reinforcing network of the hyphae and rods formed by bacteria and to the acidoid/basoid ratio of the precipitates.

The investigation describes the method in most general use against the rust precipitates to date, based on the use of copper. The principle of this

method is to destroy the bacteria and thus prevent the biological precipitation of iron. An attempt is made to elucidate, by theoretical interpretation based on laboratory experiments, the effect of copper on the equilibrium of iron. It is found that copper reduces trivalent iron to bivalent iron and, furthermore, precipitates trivalent iron in the form of ferric hydroxide. The precipitating effect is assumed to be due to the tendency of copper to form negative complex ions. The phenomenon is found to be consistent with experiments carried out in the field. From this the conclusion is drawn that the use of copper in drain pipes seams to promote precipitation of iron, particularly in soils containing humus, in which the potential formation of negative copper complex ions is assumed to exceed that in soils with less

In contrast to the method of attempting to prevent the origination of rust precipitates by the use of copper in the drain pipes themselves, a new countermeasure suggested is that based on the use of lime, by which mobile iron is precipitated before it reaches the drain pipe, above the pipe system. The results obtained, both by the preliminary field test and over a more extensive area where drainage was constructed by using this method, were relatively positive.

No final evaluation can as yet be made of the method proposed, because of the risks entailed at a later stage by the use of lime and because of the short duration of the experiments. On the strength of the theoretical study detailed in the investigation, itself based on experiments, the method can be recommended for practical purposes even at this stage.

References

AARNIO, B. 1915. Über die Ausfällung des Eisenoxyds und der Tonerde in finnländischen Sand- und Grusböden. Geotekn. medd. 16, 1-76.

ASCHAN, O. 1907. Die Bedeutung der wasserlöslichen Humusstoffe (Humussole) für die Bildung der See- und Sumpferze. Zeitschr. f. prakt. Geologie 15, 56-62. CHOLODNY, N. 1926. Die Eisenbakterien. Jena 1926. 29 pp.

CORNEY, G. W. & SCHOLLENBERGER, C. J. 1928. The effect of weathering on exchangeable bases as shown in the Clermont silt loam profile, Proceedings and papers of the first internat. congr. of soil sci., 212-229.

Dorf, Paul. 1932. Järn- och manganutfällningarna i Svartökärr. Sv. mosskulturför.

Engelhardt, J. H. 1949. Grondverbetering. Eerste deel. Batavia 1949. 152 pp.

Feilberg, AA. & Feilberg, C. L. 1921. Kulturteknisk vandbyggning. Khvn 1921.

FLODRVIST, HERMAN & GUSTAFSSON, YNGVE. 1938. Hydrologische Forschungen I. Studien über Grundwassereinströmungen durch die Fugen der Dräneleitungen. Ann. der landwirtschaftl. Hochschule Schwedens. 5, 131-164. FRECKMANN, W. 1931. Meliorationsmassnahmen. Blanck: Handbuch der Bodenlehre

9, 1-92.

Halvorson, H. O. 1931. Studies on the transformations of iron in nature: III. The effect of CO2 on the equilibrium in iron solutions. Soil sci. 32, 141-165. IGNATIEFF, V. 1941. Determination and behavior of ferrous iron in soils. Soil sci.

51, 249-263.

JENSEN, Hs. 1938. Om forhindring af okkerdannelse in drainrør. Hedeselsk. tidsskr. 59, 139-143.

JENSEN, HJALMAR & JAKOBSEN, J. M. 1946. Om forhindring af okkerdannelse in drainrør ved hjælp af kobber. Hedeselsk. tidsskr. 5, 81-86.

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Keso, Lauri. 1940. Ojaetäisyyskoe urpasavimaalla. Suomen Maataloustieteellisen scuran julkaisuja 42, 2, 1-34. LANGISCH, E. 1930. Neues Dränverfahren in eisenschussigen Böden. Der Kultur-

techniker 33, 587-588.

Mann, H. B. 1930. Availability of manganese and of iron as affected by applications of calcium and magnesium carbonates to the soil. Soil sci. 30, 117-133. MATTSON, SANTE. 1930. The laws of soil colloidal behavior: III. Isoelectric precipi-

tates. Soil sci. 30, 459-495.

1931. The laws of soil colloidal behavior: IV. Isoelectric precipitates. Soil sci. 31, 57-77. Schledermann-Larsen, C. V. 1949/50. Lidt forskelligt om dræningsforsøgsvirksom-

heden i Danmark. Grundförbättr. 1, 1-14.

STARKEY, R. L. & HALVORSON, H. O. 1927. Studies on the transformations of iron in nature: II. Concerning the importance of micro-organisms in the solution and precipitation of iron. Soil sci. 24, 381-402.

TURNER, P. E. 1931. Replaceable iron and aluminium in soils. Soil sci. 32, 447—458. WIKLANDER, LAMBERT. 1945. Om järnutfällning i täckdiksledningar. Lantbr.akad.

tidskr. 84, 358-367.

Wiklander, Lambert & Hallgren, Gunnar & Brink, Nils & Jonsson, Ernst. 1950. Studies on gyttja soils. Ann. agr. coll. Sweden, 17, 21-36.

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