Pitting of Copper Pipes in Domestic Water Systems in the UK

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Abstract

Pinholing of copper pipework in domestic cold water systems is usually attributed to either type 1 pitting or MIC, sometimes referred to as type 3 pitting. This paper looks at over 40 cases of these cases investigated by the author over the last 15 years in the UK. The morphology of the pitting is described along with the water composition, types of buildings affected and time to failure.

The locations of the cases have been plotted on a geographical map of the UK showing also water hardness. It has been found that while type 1 pitting occurs overwhelmingly in the south and east of the UK where water supplies are predominantly from hard borehole waters, type 3 pitting occurs over a much greater geographical area of widely differing water compositions. However, many other cases are not clearly of type 1 or type 3 and have characteristics of both. These are described as type 1/3. Several cases of 'blue water' in copper pipework systems due to spalling off of a modified carbonate patina have also been found to occur in soft water areas in the north of England.

Keywords

Copper; pitting; type 1; MIC; Influencing factors

Introduction

Although copper pipes in domestic cold water systems, i.e. drinking water systems, have been used successfully for 100's of years, instances of pinholing due to pitting corrosion still occur from time to time. This is usually due to either type 1 pitting or MIC (microbially induced corrosion). Type 2 pitting only very rarely occurs in hot water pipes at temperatures >60°C and therefore is not covered here. Nor is the phenomenon of erosion corrosion, which occurs predominantly in hot water systems, discussed in this paper.

When leaks occur, not only does this often necessitate costly replacement of the pipework, but it can often result in substantial water damage in buildings. In the UK, we at Midland Corrosion Services have been investigating pitting of copper pipework in hospitals, commercial office buildings, schools and large country houses for the last 18 years. When failures occur it is usually due to a combination of adverse circumstances in water composition; design and installation and operating conditions. In this paper, the morphology of the attack along with the types of buildings affected, time to failure and influencing factors are discussed for over 50 cases of type 1 and MIC pitting and blue water. These findings are summarized in Appendix 1. A map of the UK showing the distribution of all these cases alongside a map showing water hardness values is given as Appendix 2.

Overview of Pitting of Copper Pipes in Cold Water Systems

Type 1Pitting

Type 1 pitting is probably the most common form of pitting found to occur in copper tubes. It is only found in copper pipes in cold, hard bore hole (well) waters of a certain composition. Much work was carried out into this phenomenon by British Non-Ferrous (BNF) Metals Research Association in the 1960's and 1970's. They found that type 1 pitting did not occur in surface waters due to the presence of naturally occurring organic inhibitors. It was found to be promoted by the presence of carbon films left over from the pipe extrusion process. Since the introduction of EN1057, which requires the removal of the carbon films after extrusion, the incidences of type 1 pitting decreased significantly. However, it can still occur even when no carbon film residues remain on the bore of the pipe.

Type 1 pitting can result in pinhole leaks in cold water pipes any time from a few months to a few years. Mounds of green or blue/green copper hydroxycarbonate are formed above the pit sites. When these are removed by cleaning with acid, usually hemispherical pits are revealed sometimes containing crystals of white needle-shaped copper chloride and ruby red copper I oxide [1].

Most theories of pitting propose a small anode surrounded by a large cathode. However, Lucey showed that there was a large amount of calcium carbonate precipitated on the mound above the pit, indicating that cathodic activity was taking place here [2]. In addition, since there was always a membrane of copper oxide across the mouth of the pit, he proposed the membrane theory of pitting. In the mechanism, copper I chloride within the pit is anodically oxidized to copper II chloride on the underside of the oxide membrane and these ions then further attack the copper metal within the pit to reform copper I oxide. The cathodic reaction involving the reduction of oxygen to hydroxyl ions takes place on the upper surface of the membrane.

The shape of type 1 pits is usually approximately hemispherical. However, in an internal BNF report [3], Lucey went further in describing the shape of the pits seen – 'The driving force for the corrosion cell is the potential difference existing between the two faces of the oxide membrane; electrons flow through the oxide from the inner to the outer surface and the circuit is completed by the ionic path – the electrolyte solution present in the holes and pores in the oxide. However, an alternative current path is available through the metal and involves two other possible electrode reactions….'. Thus, as well as the formation of hemispherical pits if the ionic path is completely through the membrane, either a confined annulus of anodic attack or unrestrained outward spread of anodic attack is possible, as shown below in Figs. 1 and 2.

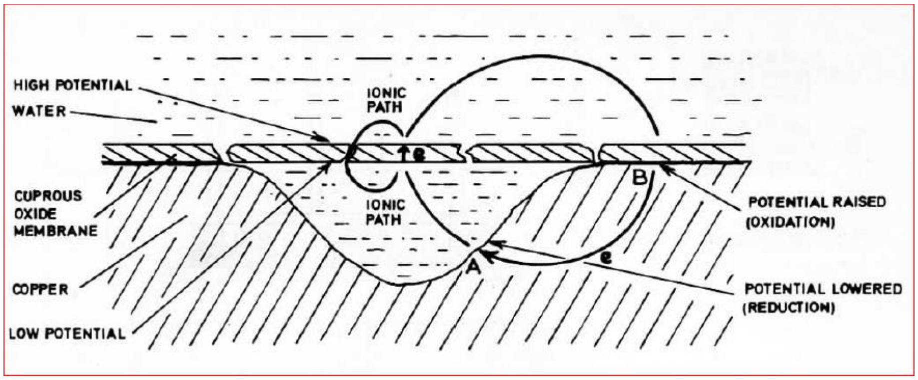

Fig.1 Possible ionic paths affecting dissolution through action of a membrane cell according to Lucey [3].

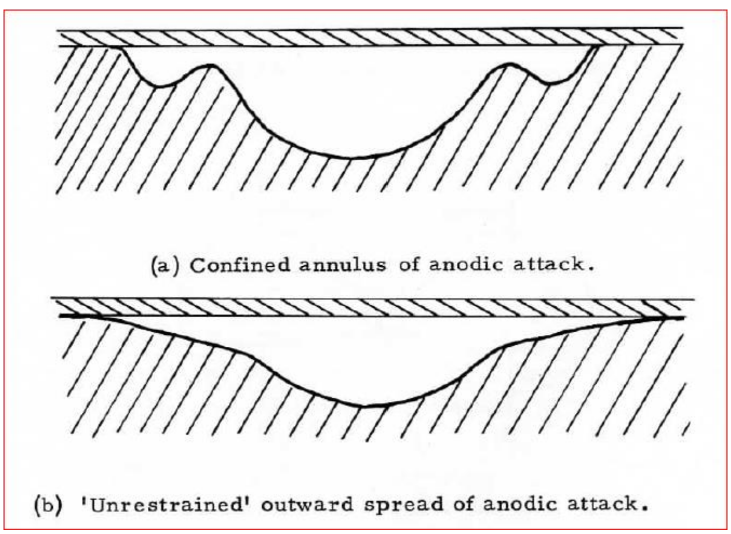

Fig. 2 Types of possible pit cavities formed, according to mechanism proposed by Lucey

A review of the effect of water composition on type 1 pitting has been produced by Francis [4]. Since water composition obviously played an important role in the determining whether or not type 1 pitting occurred, a lot of work was carried out at BNF Metals to determine what made a water a so-called pitting water. By investigating over 100 pitting and non-pitting waters in the

UK, Lucey derived empirically a nomogram based on 6 factors including pH, chloride, sulphate, nitrate, sodium and dissolved oxygen [4]. From this a pitting propensity ratio (PPR) was obtained. Those with a positive PPR were deemed pitting waters while pitting was found not to occur in waters with a negative PPR. Very aggressive waters where failure could be expected in less than 3 years had a PPR>2. Increasing dissolved oxygen, sulphate and sodium increased the PPR while increasing chloride, nitrate and especially pH decreased it. Edwards [5] has carried out more recent work and showed that increasing sulphate and nitrate promoted pitting while both increasing chloride and bicarbonate decreased it. The finding that nitrate promoted pitting was the only factor that disagreed with the findings by Lucey.

Since the work on the effect of water composition on pitting was carried out at BNF Metals, water companies in the UK have been routinely dosing ortho-phosphate into the supply waters in order to reduce the leaching of lead from old lead distribution pipework. Munn [6] has reported on how the phosphate becomes incorporated into the carbonate patina on copper pipework resulting in it becoming blue in colour and more irregular and less stable. This was found to increase the likelihood of so-called blue water but also appeared to increase the likelihood of type 1 pitting. An example of a pipe exposed to high levels of phosphate in the water is shown in Fig. 3 which contrasts with the appearance of a regular smooth green carbonate scale containing no phosphate (Fig. 4).

Fig. 3 Irregular phosphate-containing carbonate deposit on bore of cold water pipe

Fig. 4 Regular green carbonate patina formed on cold water pipes

Finally, although pitting caused by soldering flux is usually regarded as a form of attack in its own right, Edward [5] has argued that anything that creates an excess of copper I chloride on the copper pipe such as soldering fluxes may initiate type 1 pitting.

MIC

Microbial Influenced Corrosion of copper is sometimes referred to as type 3 pitting (type 2 pitting is a completely separate form of pitting, which only occurs in hot water pipes above 60°C). Type 3 form of pitting may appear similar to type 1 pitting on first inspection, i.e. with nodules of copper carbonate predominantly on the bottom of horizontal pipe runs, although it sometimes appears as large irregular-shaped mounds of carbonate along the bottom of pipes. Within the carbonate mounds, however, often copper hydroxyl sulphate is present. Surrounding these areas of attack, the surface is usually covered with a black layer of copper II oxide (cupric oxide).

Present within the deposits above the copper surface, is usually a biofilm containing polysaccharides, secreted by micro-organisms, esp. pseudomonas [7]. The physico-chemical properties of the biofilm are considered to play an essential role in the MIC process [8].

A classic form of MIC is the presence of a high density of tiny pits, known as 'pepper-pot corrosion' underneath the surface layers. However, they can also appear as hemispherical pits surrounded by or coalescing with much smaller pits. Walker et al [9] proposed that the 'pepper-pot' pitting found in Scottish hospitals was due to the creation of oxygen differential cells with low oxygen beneath the biofilm so that the 'pepper-pot' pitting was essentially the footprint of the microcolony structure within the biofilm. However, it is also quite likely that anaerobic bacteria, especially sulphate reducing bacteria (SRB) can rapidly develop beneath biofilms. It is the formation of acid and HS by the metabolism of SRB, which then can cause localized attack of the copper.

Type 3 pitting or MIC has been reported in Germany, Sweden, Australia, Japan and the UK [10]. All appeared to occur in cold or hot water pipes but where the water temperatures in that section of pipework was between 25 and 50°C. All the waters were reported to be soft with a low pH but with other factors contributing.

The time to failure of copper pipes due to MIC tends to be longer than for type 1 and unlike the latter, the frequency of failures does not appear to decrease with time, at least over the first 10 years [11]. However, the likelihood of both type 1 and MIC pitting occurring is greatly increased if water is allowed to stagnate in the pipes for long periods.

Tests carried out on pipes and water samples

Pipe samples when they are received are sectioned longitudinally and the nature and colour of the patina and presence, shape and size of nodules recorded after inspection with the naked eye. Small pieces of the pipe are tested for the presence of carbon film residues and biofilms by immersing for a short time in 25% nitric acid. Biofilms appear as gelatinous, transparent films often attached to gas bubbles floating in the acid (see Fig. 5). A staining test for polysaccharides using periodic acid-Schiff reagent may also be carried out [12]. If black flakes are also observed, the acid is then boiled for 3 minutes in order to dissolve any black copper oxide. Any black flakes remaining would then be insoluble carbon.

A sodium azide/iodine spot test is carried out to determine whether or not sulphide is present in any nodules. The presence of sulphide is good evidence for the activity of SRB, as sulphides are not normally present in drinking water. The presence of sulphide is revealed by the evolution of nitrogen gas bubbles when viewed under an optical microscope, as shown in Fig. 6.

After cleaning the bore and any nodules with 10% sulphuric acid, the morphology of any attack on the underlying copper is revealed by inspection under an optical zoom microscope.

Water samples are analysed by ICP and other physico-chemical means usually within 3 days of sampling.

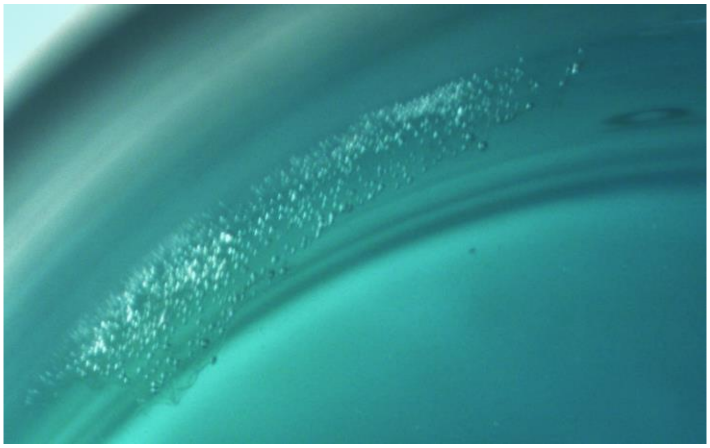

Fig. 5 Typical appearance of biofilm extracted from bore of copper pipe

Fig. 6 Nitrogen gas bubbling indicating presence of sulphides
in deposits in sodium azide/iodine spot test

Morphology of Pitting Observed

When inspecting the nature of the pitting attack on copper pipes before and after cleaning, it is not always immediately clear whether the attack is type 1 or due to MIC. The variations in the morphology of attack observed is shown in examples from the cases studied in Figures 7- 18.

Very few pits are found to be perfectly or even nearly hemispherical, i.e. classic type 1 pits. Figs. 7b and 8b show approximately hemispherical pits, which are clearly type 1. The nodules of copper hydroxycarbonate on the pipe bore are usually located close to the bottom of the pipe and often are elongated due to streaming copper I chloride corrosion products under the action of gravity. A x-section through another type 1 pit from the same case as shown in Fig 8b is shown in Fig. 8c. Here, the copper oxide membrane separating the carbonate mound on top of the pit from the pit in the copper is clearly seen. Note that the pit cavity itself contains several smaller hemispherical pits. A similar looking x-section is shown in Fig. 9b. In this case, widespread pitting attack was found under longitudinal streaks of carbonate along the bottom of the bore.

A variation on the shape of a type 1 pit with several rings of attack around a deep central pit is shown in Fig. 10b. The formation of this shape of pit was explained by Lucey when the current path between anode and cathode also passed through the surrounding copper rather than just the copper oxide membrane.

Often elongated mounds of carbonate are found close to the bottom of the pipe. When this is cleaned away, multiple large and small hemispherical pits are revealed, as shown in Fig. 11. Around the edge of some roughly hemispherical deep pits, there are multiple smaller pits, as shown in Fig. 12b.

Classic type 3 or MIC pits look completely different to the above examples. Although the carbonate mounds on the bore may look similar to those found with type 1 pits, as shown in Fig. 13a, once these have been removed by cleaning with acid, the underlying attack does not show any large single pits with or without small hemispherical pits. Instead, one sees irregular-shaped steep-sided pits with often multiple smaller deep satellite pits (Fig. 13b). Other clear examples of MIC pits with ‘pepper-pot’ pitting are shown in Figs. 14 and 15. In these cases, often the bore contains black copper II oxide or other deposits.

Three examples are shown where the type of pitting is not clear (Figs. 16, 17 and 18). When viewed with the naked eye, the pitting on the bore does appears like type 1. However, the individual pits are found to contain or be surrounded by multiple very small pits, which resemble ‘pepper-pot’ attack.

In order to made a decision as to whether there has been any microbial influence on the pitting seen, further tests including tests for biofilm and sulphide have been made.

Fig. 7a – Case 4 Type 1 pitting – bore before cleaning

Fig. 7b – Case 4 Type 1 pitting – close up of pit

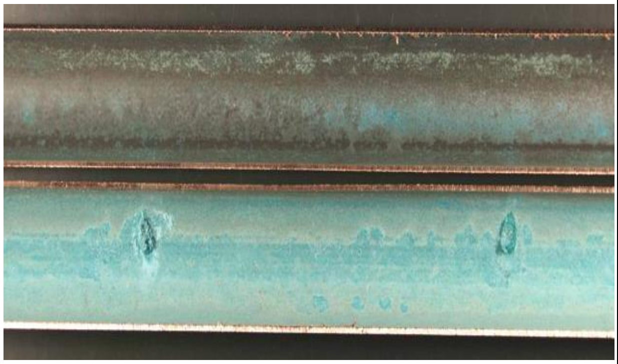

Fig. 8a – Case 15 Type 1 pitting -bore before cleaning

Fig. 8b – Case 15 Type 1 pitting – close up of pit

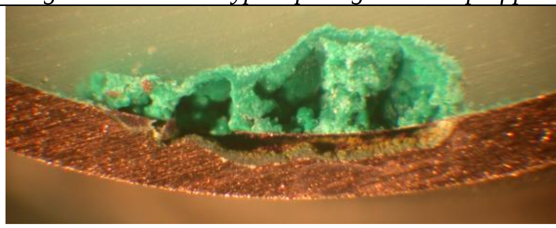

Fig. 8c – Case 15 x-section through pit

Fig. 9a – Case 23 Type 1 pitting -bore before cleaning

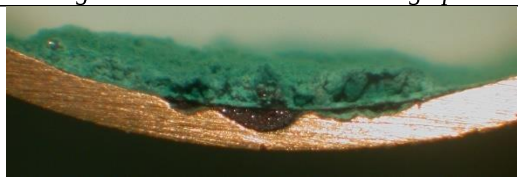

Fig. 9b – Case 23 X-section through type 1 pit

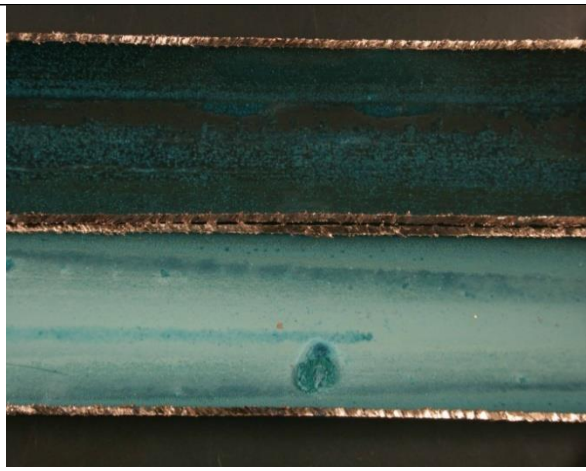

Fig. 10a – Case 7 Type 1 pitting -bore before cleaning

Fig. 10b – Case 7 Type 1 pitting – close up of pit

Fig. 11a – Case 30 Type 1 pitting -bore before cleaning

Fig. 11b – Case 30 Type 1 pitting – close up of pit

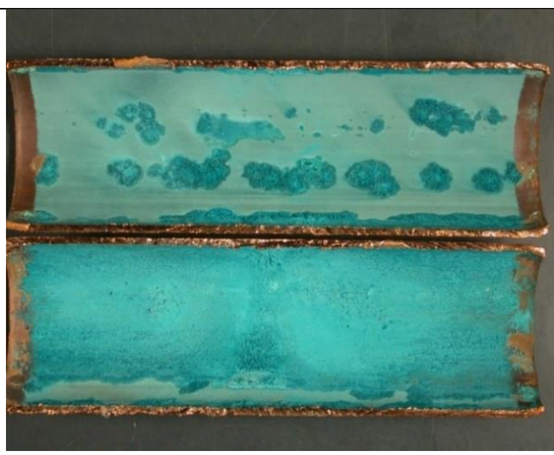

Fig. 12a – Case 8 Type 1 pitting -bore before cleaning

Fig. 12b – Case 8 Type 1 pitting – close up of pit

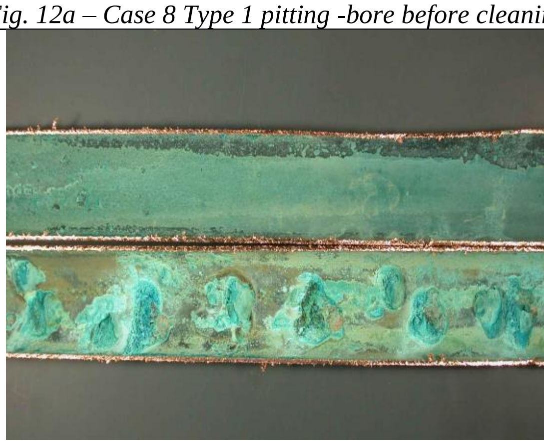

Fig. 13a – Case 3 MIC pitting -bore before cleaning

Fig. 13b – Case 3 MIC – pepper-pot corrosion

Fig. 14a – Case 10 MIC pitting -bore before cleaning

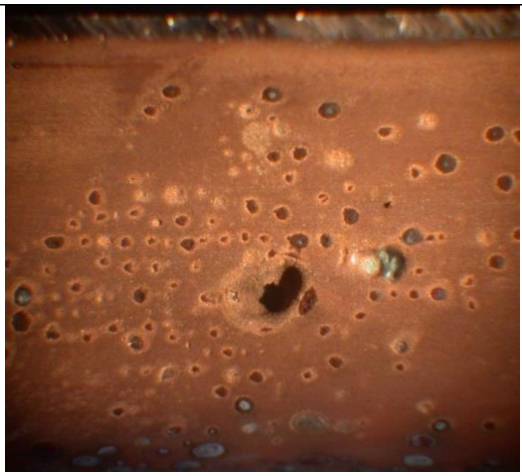

Fig. 14b – Case 10 MIC – pepper-pot corrosion

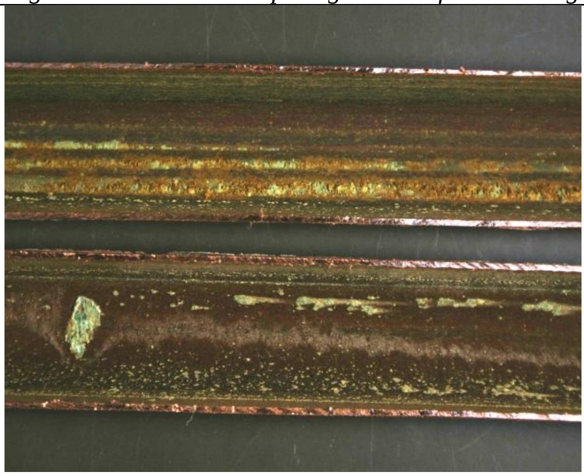

Fig. 15a – Case 9 MIC pitting -bore before cleaning

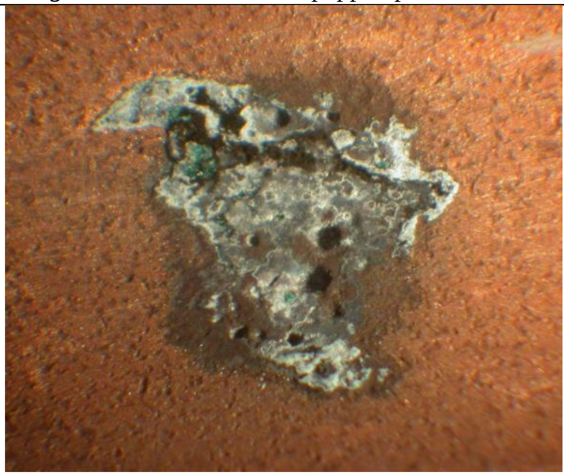

Fig. 15b – Case 9 MIC pitting -pit after cleaning

Fig. 16a – Case 16 - bore before cleaning

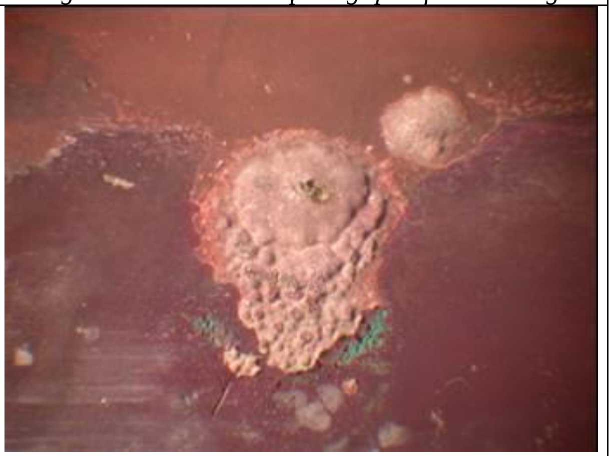

Fig. 16b – Case 16 - pits after cleaning

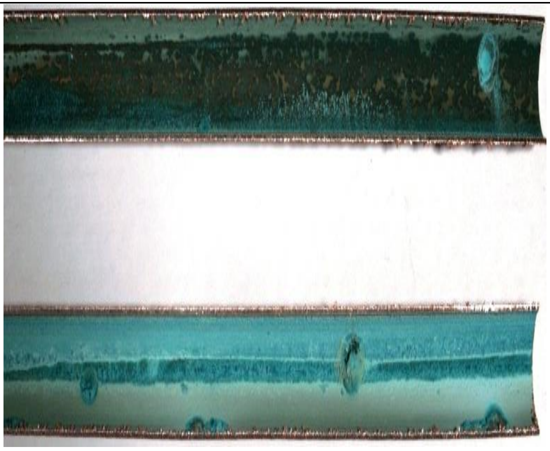

Fig. 17a – Case 20 - bore before cleaning

Fig. 17b – Case 20 - pit after cleaning

Fig. 18a – Case 21 - bore before cleaning

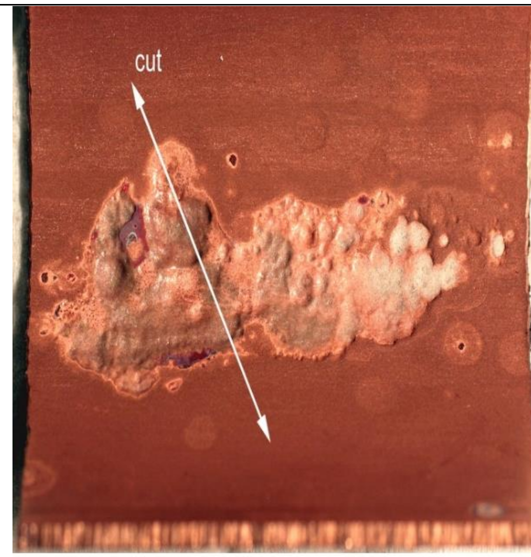

Fig. 18b – Case 21 - pit area after cleaning

Factors Influencing Pitting and Times to Failure

Carbon Films

Out of 20 cases of clear type 1 pitting where the pipes were tested for carbon film residues, 5 were deemed positive, i.e. 25%. Therefore, it is apparent that, although the presence of carbon films may increase the likelihood of pitting, they are not a pre-requisite for this form of pitting to occur.

Water Composition

Tables 1 and 2 show some key parameters from the water analysis results (in cases where analysis had been carried out on the supply waters) for cases which were clearly of type 1 and MIC pitting. These are: pH, M (total) Alkalinity, chloride, sulphate and phosphate. Ratios of sulphate:chloride and sulphate:alkalinity have been determined, as these ratios may be more important that the actual value of each parameter. In addition, the PPR values have been calculated using a software program derived from the nomogram developed by BNF Metals. The PPR value is particularly sensitive to pH. Since it has been found that the pH of some waters can increase by up to 0.4 units between sampling and laboratory analysis several days later, PPR values have been calculated using the pH measured by the laboratory and also at 0.4 pH units less than the lab recorded value. In these calculations a dissolved oxygen of 8mg/L (ppm) was used, which is close to saturation at 15°C.

CASE No	pH	Total Hardness (mg/L as CaCO3)	M Alkalinity (mg/L as CaCO3)	Chloride (mg/L)	Sulphate (mg/L as SO4)	[SO4:Cl]	[SO4:Alk]	Phosphate (mg/L as PO4)	PPR (pH as given)	PPR (pH as given- 0.4)
1	7.4	9.4	160	76	51	0.67	0.32	4.5	2.1	5.6
2	7.6	452	310	44	189	4.30	0.61	3.3	5.4	8.9
4	8.1	393	260	52	71	1.37	0.27	0.6	-2.4	-0.8
7	7.7	320	293	25	39	1.56	0.13	9.3	0.1	2.7
8	7.5	260	210	41	50	1.22	0.24	3.3	-0.7	2.1
11	7.8	362	255	79	76	0.96	0.30	0	-1.6	1.0
12	7.7	262	253	55	56	1.02	0.22	1.5	-2.4	0.2
13	7.6	337	311	71	124	1.75	0.40	3.3	0.1	3.0
14	7.7	285	237	33	46	0.19	0.19	4.2	-1.6	1.0
17	8.0	268	255	13	32	0.13	0.13	0	-1.3	0.5
19	8.1	260	280	38	45	1.18	0.16	3	-0.4	0.2
20	7.4	252	202	38	46	0.18	0.23	1.2	2.3	6.5
23	7.5	249	210	14.5	9.1	0.63	0.04	0.3	-6.4	-4.1
24	8.2	0.9	245	19	77	4.05	0.31	1.2	8.9	10
25	7.7	327	245	56	74	1.32	0.30	5.6	-0.2	0.6
28	8.0	260	191	51	48	0.94	0.25	4.8	-3.2	-1.1
34	7.7	432	301	37	138	3.73	0.46	1.5	3.4	6.0
38	6.8	344	268	77	50	0.65	0.19	3.2	7.5	10
No	18	18	18	18	18	18	18	18	18	18
mean	7.7	281.9	249.2	45.5	67.8	1.4	0.3	2.8	0.5	2.9
min	6.8	249*	160.0	13.0	9.1	0.1	0.0	0.0	-6.4	-4.1
max	8.2	452.0	311.0	79.0	189.0	4.3	0.6	9.3	8.9	10.0

*excluding cases 1 and 24 where softened water was used

Table 1 Water Parameters for Cases of Type 1 Pitting

CASE No	pH	Total Hardness (mg/L as CaCO3)	M Alkalinity (mg/L as CaCO3)	Chloride (mg/L)	Sulphate (mg/L as SO4)	[SO4:Cl]	[SO4:Alk]	Phosphate (mg/L as PO4)	PPR (pH as given)	PPR (pH as given- 0.4)
3	6.9	147	120	39	68	1.74	0.57	0	8.1	>10
9	7.2	32	53	11	36	3.27	0.68	34	6.8	<10
16	7.2	283	260	34	48	1.41	0.18	1.5	1.3	6.5
18	7.0	2.6	312	49	32	0.65	0.10	0	>10	>10
21	7.6	101	192	23	21	0.91	0.11	0	-1.2	2.3
29	7.9	384	216	52	50	0.96	0.23	4.2	-3.1	-1.1
35	7.2	162	267	33	32	0.97	0.12	0.3	-1.7	3.5
36	7.8	357	293	48	28	0.58	0.10	3	-4.4	-2.1
37	6.7	24	21	4.9	4.7	0.96	0.22	2.4	9.1	>10
41	6.9	22	132	60	121	2.02	0.92	6.3	4.8	>10
No	10	10	10	10	10	10	10	10	9	10
mean	7.2	151.5	186.6	35.4	44.1	1.3	0.3	5.2	2.2	1.8
min	6.7	2.6	21.0	4.9	4.7	0.6	0.1	0.0	-4.4	-2.1
max	7.9	384.0	312.0	60.0	121.0	3.3	0.9	34.0	9.1	>10

Table 2 Water Parameters for Cases of MIC (Type 3) Pitting

For **type 1 pitting**, the water hardness was always at or above 250mg/L as $CaCO_3$ (except in cases 1 and 24 where the water had been softened) and clearly derived from borehole water. Since type 1 pitting had also occurred in 2 cases with softened water, it is apparent that base-exchange softening of the water does not prevent type 1 pitting occurring. The pH ranged from 6.8 to 8.2 with the large majority between pH 7.4 and 8.0.

Chloride and sulphate levels appeared within the normal range but the ratio of sulphate:chloride varied greatly from 0.1 to 4.3. Therefore, one can say that the ratio of sulphate:chloride is not important here. Although other researchers have suggested that pitting is more likely with a high sulphate:alkalinity ratio, at least for the type 1 pitting cases studied here, we found no correlation except that the sulphate:alkalinity ratio was always <0.6.

PPR values derived using the lab measured pH varied greatly from -6.4 to 8.9 with a mean of 0.5. When using the lower adjusted pH, the range in PPR was from -2.1 to >10. In addition to this wide variation, we found no correlation between the time to failure (as shown in Appendix 1) and the PPR values, as proposed by Lucey and Campbell.

The concentration of phosphate in the water (dosed by water companies) was above 3mg/L (as PO_4) in 10 and above 1 mg/L in 14 of the 18 cases where water analysis had been carried out. In these and in most other cases where water analysis had not been carried out, the carbonate patina was found to be blue or turquoise in colour. EDX analysis has shown high levels of phosphate incorporated into the patina in these cases, while the more regular green copper hydroxycarbonate patina contains no phosphate.

For clear **MIC (type 3) pitting**, the water hardness ranged from 22 to 384mg/L as $CaCO_3$ (except for case 18 where softening of the supply water had taken place). Although the mean in water hardness and pH was less than for the type 1 cases, this work does not support the view that type 3 or MIC pitting predominantly occurs in soft water of low pH. Both chloride and sulphate levels were on average lower than in the cases of type 1 but the mean ratio of sulphate:chloride was found to be about the same type 3 and type 1 at 1.3 and 1.4, respectively.

As with the type 1 cases, the calculated PPR values were found to vary widely from -4.4 to >10 when using the lab recorded pH values. Therefore, it is clear that, as expected, PPR values do not indicate whether MIC pitting is likely to occur or time to failure if it does occur.

High phosphate levels above 3mg/L were found in 4 of the 10 cases where water analysis was available and above 1mg/L in 6 of the 10 cases.

In the 8 cases of **blue water** investigated, all were in soft water areas and nearly all had high levels of phosphate in the water (see Appendix 1). This resulted in a blue, irregular and unstable patina, an example of which is shown in Fig. 4.

Discussion

The numerous investigations into pitting of copper cold water pipes in the UK carried out in our laboratory over the last 15 years or so, have indicated that pinholing not only can be due to clear type 1 pitting or MIC pitting but that many pitting cases have characteristics of both. Thus, the copper bore may exhibit tiny deep pits surrounding larger roughly hemispherical pits.

Biofilms may be present on the bore of pipes containing clear type 1 pits as well as on pipes with clear MIC pits. These biofilms may or not harbour sulphate reducing bacteria (as evidenced by the detection of sulphide). It could be that there are other micro-organisms besides SRB responsible for MIC. On the other hand, the growth of biofilms and SRB are only at most pre-cursors to MIC occurring and therefore one could detect these on pipes where MIC has not led to any significant pitting. Many cases we have investigated then could be classed as type 1 pitting with microbial influence, which has been classified as type 1/3.

The presence of carbon films may encourage type 1 pits to initiate, as was clear from a lot of work carried out in the 1960 and 70's. However, it is clear from our work that since the introduction of EN 1057 (which requires that carbon films are removed from the pipe bores following annealing) most cases of type 1 pitting are not due to the presence of these films.

The role of phosphate in supply waters in promoting both type 1 and MIC pitting and blue water is not clear. It is apparent from our work that phosphate was present in the carbonate patina and mounds above pit sites in the large majority of cases we have investigated. Also, it was always found in the irregular unstable carbonate patina found in cases of blue water.

The colour of the patina on the pipe bores shown in Figs. 8-18, with one exception, were blue or blue-green as opposed to a darker green characteristic of copper hydroxycarbonate without phosphate present. However, since nearly all mains water in the UK is now dosed with phosphate, this may be an associative phenomenon and not causative. Probably, most copper pipes in domestic cold water systems in the UK would exhibit a blue or blue-green patina containing phosphate but be free of any pitting. Nevertheless, newly installed pipework where the copper oxide/carbonate patina has not developed, may be particularly vulnerable to pitting if high phosphate-containing water is left to stagnate in the pipework after first filling. Once a regular compact carbonate patina has developed, it would be relatively insensitive to changes in water composition. It is important to realise that the water analysis shown here is only a spot analysis carried out months or years after the pipework was installed and therefore may be very different in composition to the original fill water.

It could be that phosphate encourages type 1 pitting because it is an anodic type inhibitor for copper leading to concentration of attack in areas where phosphate levels are much lower than elsewhere on the copper surface. In the case of MIC, it is conceivable that phosphate may also act as a nutrient for bacterial growth. More work needs to be undertaken to understand whether or not phosphate in the water increases the likelihood of pitting of cold water copper pipes and, if so, its role in causing pitting.

On other aspects of water composition, we did not find that a positive PPR value (derived from software developed using the BNF Metals nomogram) was associated with the formation of type 1 pitting nor that more positive values were linked with reduced time to failure. The reason for this is not clear, but there must be other factors involved which are much more important than the PPR value. In addition, we found no link between the [sulphate: chloride] ratio and [sulphate:alkalinity] ratio and the occurrence of both type 1 and MIC pitting with wide variations in both being apparent.

For type 1 pitting, the water was always derived from a hard bore-hole source, which is consistent with that found by others. However, for type 3 pitting, our findings would appear to conflict with findings of others, who have reported that type 3 or MIC pits always occurs in soft waters with low pH [10]. Our findings suggest that this form of pitting can occur in both hard and soft waters.

The locations of all of the cases presented here are shown on a map of the UK (mainly England) together with representation of the local water hardness is shown in Appendix 2. It is clear from this that cases of type 1 pitting are concentrated in the SE of England and up to East Anglia (e.g. Cambridge) with a few dotted around the Bristol channel. We have only investigated one case of type 1 pitting in the north of England and none in Scotland, Wales or the North West or far South West of England. Therefore, the cases of type 1 pitting correspond well with the map of water hardness for the UK.

Cases of type 3 (MIC) or those classed type 1/3, i.e. type 1 with some microbial influence, are more randomly scattered around England with many cases of type 3 occurring in the north of the country. However, we have again not had any cases of these forms of attack in either Scotland, Wales or the far South West of England.

Cases of blue water have, with only one exception, all occurred in the north of England and Scotland, where the supply waters are soft or very soft.

Finally, it has been found for all forms of pitting whether MIC or type 1, that the likelihood of this occurring is greatly increased due to water stagnation in the pipework, especially in the initial few months after installation. Water stagnation in hot water pipes could also result in either type1 or MIC occurring, since the water temperatures would fall to ambient. Temperatures between around 22°C and 45°C would encourage microbial growth and therefore could lead to MIC pitting occurring. This finding is unsurprising as it is consistent with that reported by many others.

Conclusions

The findings from 50 cases of pitting and blue water from copper pipework systems in domestic water systems in the UK investigated over 15 years have been presented. Detailed analysis has shown that:

- Pits may take the form of type 1 or type 3 (MIC) pits, although in many cases, the pits have characteristics of both forms and may be classed as type 1 pits with microbial influence or type 1/3 pits.
- Carbon film residues on the bore of pipes have been found on only around 25% of the cases of type 1 pitting investigated. Therefore, although they may promote pitting, the presence of carbon films is not a pre-requisite.

- Type 1 pitting only occurs in hard bore-hole water with cases concentrated in the south and east of England.
- Cases of Type 3 (MIC) and type 1/3 pitting occur over a very wide range of water hardness values and have been found much more widely throughout the UK.
- For both type 1 and 3 pitting, high [sulphate:chloride] and [sulphate:alkalinity] ratios and high PPR (pitting propensity ratio) values are not required to cause pitting or reduce times to failure.
- In most cases of type 1 and type 3 pitting, high levels of phosphate have been found in the water and, when analysed, in the carbonate patina on the bore of the pipes and in nodules above pits. However, it is not clear whether the phosphate plays an active role in the pitting process or is just an associative effect.
- In the large majority of cases of all pitting types studied, water stagnation in the early stages after installation of the pipework system appears to have been an important factor in causing the pitting to occur.

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Appendix 1 - CASES OF PITTING & BLUE WATER IN COPPER DOMESTIC WATER SYSTEMS

SYSTEM	Location	Building Type	Hot/Cold	Year First Appeared	Time from Installation to Failure (months)	Pitting Type	Pepper Pot	Carbon Film	Biofilm	Sulphide In deposits	PPR	Phosphate In Water (mg/L as PO4)
1	Shillington, Beds	Manor House	CW	2000/1999	36-48	1	N	?	?	?	2.1 (5.6)	4.5
2	Haverhill, Sussex	Commercial	HW/CW	2003	?	1	N	?	?	?	5.4 (8.9)	3.3
3	Kirby, Merseyside	Private house	CW	2003	120	3	Y	?	?	Yes	8.1 (>10)	0
4	Colchester	Private house	CW	2005	12	1	N	?	?	No	-2.4 (-0.8)	0.6
5	Cambridge	Laboratory	CW	2005	?	1	S	No	No	?	-	-
6	Bristol	Private Houses	HW/CW	2006	96	1	S	?	?	?	-	-
7	Harlow	Commercial	CW	2007	?	1	N	No	No	?	0.1 (2.7)	9.3
8	Richmond	Sports club	CW	2007	12-18	1	N	Yes	?	?	-0.7 (2.1)	3.3
9	Halifax	Commercial	Hot	1975	48	3	Y	No	Yes	Yes	6.8 (>10)	31.5
10	Braintree, Essex	Private house	CW	2006	36	1/3	S	?	?	?	-	-
11	Harwich, Essex	Hospital	CW	2006	5/6	1	N	Yes	?	?	-1.6 (1.0)	0
12	Ebbsfleet, Kent	Stations	CW	2007	12	1	N	Yes	?	?	-2.4 (3.0)	1.5
13	Kingston, Surrey	Hospital	CW	2008	8	1	N	Yes	?	?	0.1 (7.6)	3.3
14	Central London	Hospital	CW	2008	6	1	N	Yes	?	?	-1.6 (1.0)	4.2
15	Fareham, Surrey	Fire Call Centre	CW	2009	12	1	N	No	Yes	Yes	-4.6 (-3.3)	0.6

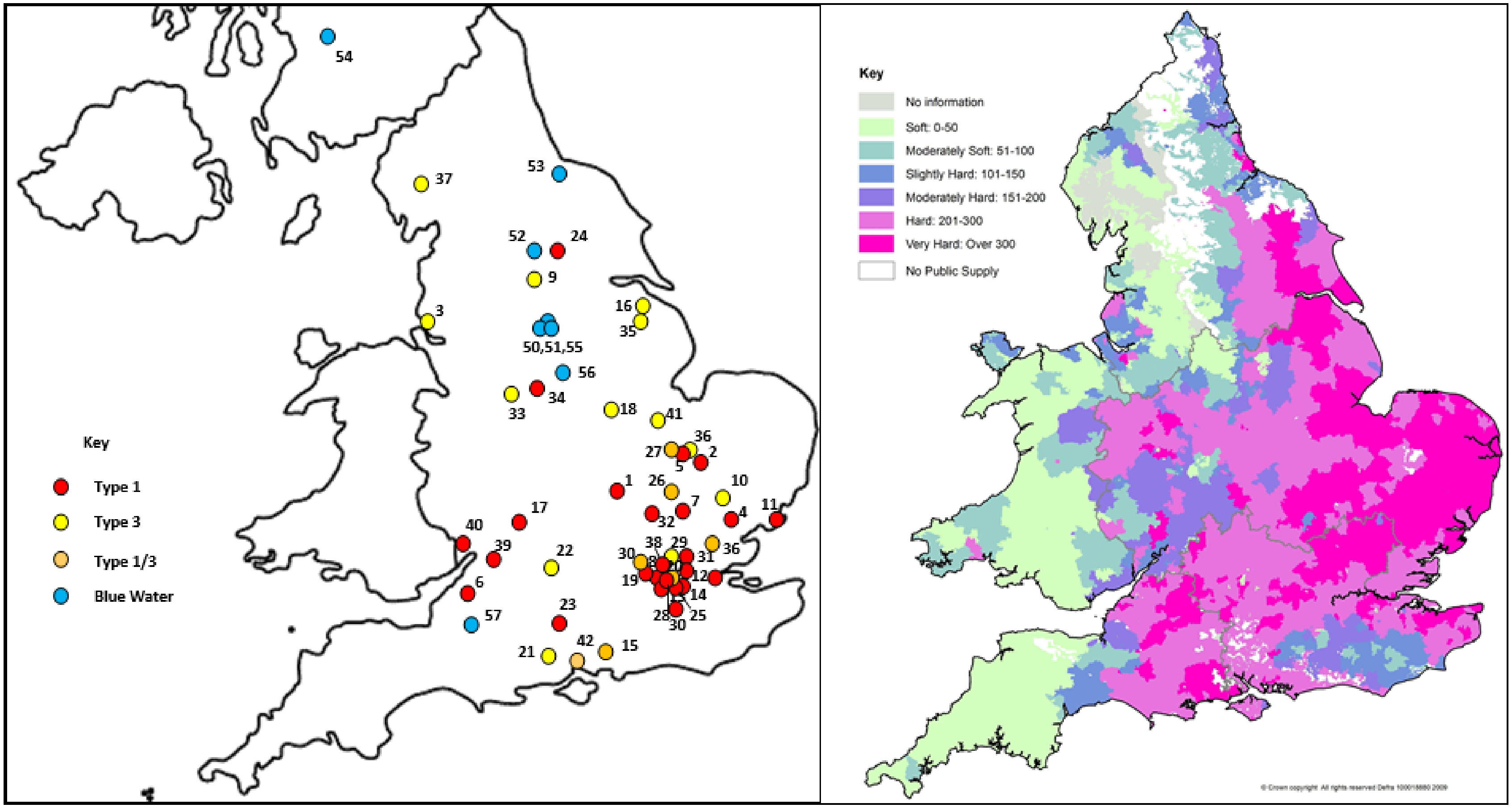
SYSTEM	Location	Building Type	Hot/Cold	Year First Appeared	Time from Installation to Failure (months)	Pitting Type	Pepper Pot	Carbon Film	Biofilm	Sulphide	PPR	Phosphate In Water (mg/L)
16	Grimsby, Humberside	School	HW/CW	2010	15	3	Y	No	Yes	?	1.3 (6.5)	1.5
17	Chipping Campden, Gloucs.	Farm	HW	2011?	?	1	N	No	No	Trace	-1.3 (0.5)	0
18	Buckminster, Grantham	Private house	CW	2012?	36-48	3	Y	No	Yes	Trace	>10 (>10)	0
19	Southall, London	School	HW	2013	42	1	N	No	No	Trace	-1.4 (0.2)	3
20	Thamesmead, London	Prison	HW	2012	12	1	N	No	Yes	No	2.3 (6.5)	1.2
21	Wimborne, Dorset	School	CW	2012	12	3	Y	No	Yes	No	-1.2 (2.3)	-
22	Swindon, Wiltshire	College	CW	2004	24	3	S	No	Yes	Yes	-	-
23	Stockbridge, Hants	Farm	CW	2009-2013	18	1	?	No	No	?	-6.4 (-4.1)	0.3
24	Wetherby, Yorkshire	Private House	CW	2012	8	1	?	No	No	?	8.9 (>10)	1.2
25	Lewisham, London	Private House	CW	2013	?	1	N	No	No	No	-2 (0.6)	5.4
26	Loughton, Essex	?	?	?	?	1/3	S	?	Yes	?	-3.0 (-1.7)	6.6
27	Cambourne, Cambs	School	CW	2014	6	1/3	S	No	Yes	Not Tested	-4.0 (-2.2)	9
28	Central London	office	HW	2013		1	N	No	No	No	-3.2 (-1.1)	4.8
29	Waltham Forest	Art Gallery	CW	2012	15	3	S	No	Yes	No	-3.1 7.9	7.2
30	Croydon	Academy	CW	?	?	1	S	No	No	No	-	Yes
31	Ruislip, Middlesex	Apartments	CW	2015	9	1/3	S	No	Yes	No	0.8 (5.7)	7.2

SYSTEM	Location	Building Type	Hot/Cold	Year First Appeared	Time from Installation to Failure (months)	Pitting Type	Pepper Pot	Carbon Film	Biofilm	Sulphide	PPR	Phosphate In Water (mg/L)
32	Letchworth, Herts	College	CW	2015	8	1	N	No	No	No	-	?
33	Forton, Staffs	Large Country House	CW	2016	?	3	Y	No	Yes	?	-	?
34	Staffordshire	Children's Home	CW	?	?	1	N	No	No	No	3.4 (6.0)	1.5
35	Ashby-cum-Fenby, Lincs	Large Country House	CW	2017	84	3	Y	No	Yes	Yes	-1.7 (3.5)	No
36	Cambridge	Student Accommodation	CW	?	?	1/3	S	No	Yes	Yes	-4.4 (-2.1)	3.0
37	Ambleside, Cumbria	Holiday Flats	CW	2017	100	3	Y	No	No	Yes	9.1 (>10)	2.4
38	Northwood, Middlesex	Block of flats	CW	2017	?	1	N	No	No	No	7.5 (>10)	4.2
39	Wooton-u-Edge, Gloucs	Large country house	CW	2018	30	1	N	No	No	No	-	No
40	Forest of Dean	Large Country House	CW	2018		1	N	No	No	No	-	33
41	Peterborough, Cambs	Large Country House	CW	2009	600	3	Y	No	Yes	Yes	4.8 (>10)	2.1
42	Southampton	University	CW	2018	24	1/3	S	No	Yes	No		5.4

CASES OF BLUE WATER

SYSTEM	Location	Building Type	Hot/Cold	Year First Appeared	Time from Installation to Failure (months)	Pitting Type	Phosphate In Water (mg/L)
50	Whirlow, Sheffield	Large Private house	HW/CW	2001	6	BW	**5.3**
51	Totley, Sheffield	Large Private houses	HW/CW	2001	24	BW	**?**
52	Ilkley, West Yorkshire	School	CW	2002	18	BW	**0.6**
53	Durham	School	CW	2004	6	BW	**20.7**
54	East Kilbride, Glasgow	College	CW	2008	13	BW	**4.2**
55	Totley, Sheffield	School	CW	2010	60	BW	**2.7**
56	Loughborough, Leicestershire	University labs	CW	2010	?	BW	**3.3**
57	Castle Cary, Somerset	Private House	CW/HW	2016	?	BW	**2.4**

Appendix 2 - MAP OF UK SHOWING LOCATIONS OF CASES OF PITTING AND BLUE WATER



1	Shillington Beds	15	Fareham, Surrey	29	Waltham Forest, London	50	Whirlow, Sheffield
2	Haverhill, Suffolk	16	Grimsby, Humberside	30	Croydon, Surrey	51	Totley, Sheffield
3	Kirby, Merseyside	17	Chipping Campden , Glouc.	31	Ruislip, Middlesex	52	Ilkely, West Yorkshire
4	Colchester, Essex	18	Buckminster, Grantham, Lincs	32	Letchworth, Herts	53	Durham, co. Durham
5	Cambridge, Cambs	19	Southhall, London	33	Forton, Staffs	54	East Kilbride, Glasgow
6	Bristol	20	Thamesmead, London	34	Staffordshire	55	Totley, Sheffield
7	Harlow, Essex	21	Wimborne, Dorset	35	Ashby-cum-Fenby, Lincs	56	Loughborough, Leicestershire
8	Richmond, London	22	Swindon, Wiltshire	36	Cambridge	57	Castle Cary, Somerset
9	Halifax, W. Yorkshire	23	Stockbridge, Hants	37	Ambleside, Cumbria		
10	Braintree, Essex	24	Wetherby, W. Yorks	38	Northwood, Middlesex		
11	Harwich, Essex	25	Lewisham, London	39	Wotton-u-Edge, Gloucestershire		
12	Ebbsfleet,	26	Loughton, Essex	40	Newland, Forest-of Dean		
13	Wiltshire	27	Camborne, Cambs	41	Peterborough, Cambridgeshire		
14	Central London	28	Central London	42	Southampton		