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Research

Creep of the Copper Canister

A Critical Review of the Literature

William H Bowyer

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SKI perspective

Background and purpose of the project

The integrity of the canister is an important factor for long-term safety of the repository for spent nuclear fuel. When the canister is placed in the repository hole it will be subjected to mechanical loads due to the hydrostatical pressure and the swelling pressure of the bentonite surrounding it. Copper is a soft material and will creep and lay down on the ductile iron insert due to the loads. The creep process will go on until the bentonite is fully saturated. During this time period the creep properties of the copper canister are very essential for its integrity. The copper material may creep but is not supposed to fracture. SKB has investigated the creep properties of the used copper material (Oxygen Free Copper with 40 – 60 ppm phosphorous, OFP material), by carrying out different research projects regarding creep.

To be able to conclude the results of these projects and take a fair stand about the need of further investigations about this matter, SKI has by this project made a literature review of the results presented by SKB.

The project uses the results presented in research projects regarding creep of copper carried by SKB.

Results

The most important conclusion is that in spite of the huge amount of research projects carried out by SKB, it is not proved that OFP material will have satisfactory creep properties in the stress region of interest in the repository.

Effects on SKI work

The study will be a basis for coming SKI research projects and SKI reviews of SKB’s RD&D-programme.

Project information

Responsible for the project at SKI has been Behnaz Aghili.
SKI reference: 14.9-010625/01106.

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Contents

Summary

Literature relevant to creep of the copper shell of the copper-iron canister has been reviewed.

Two classes of copper have been examined, Oxygen Free High Conductivity (OFHC), which is referred to in the relevant literature and this report as OF material, and OF material with 50 ppm of phosphorus added. The second material is referred to as OFP.

Creep processes occurring in copper are briefly described and a deformation diagram, after Frost and Ashby (1982) is provided. It is concluded that the diagram adequately describes the processes observed for the two materials of interest without necessarily being in exact agreement at a quantitative level.

There are two regimes of time, temperature and stress which are important when creep of the copper shell is considered. The first is a holding period between welding of the lid to the canister and placing the canister in the repository and the second is the storage period in the repository.   In the holding period, residual stresses arising from the manufacturing processes are important and in the second period stresses arising from repository pressures are important as well as the residual pressures arising from manufacture.

The holding period may extend up to one year and the temperature of the copper shell may decline from the immediate post welding temperature to 100 ºC in this interval. Initial peak localised stresses may give rise to strains of up to 14 %. Dynamic recovery immediately after welding reduces the stresses associated with these strains to levels which correspond to stresses for approximately 0.1 % strain at the ruling temperature. This is 75 MPa at 100 ºC and 50 MPa for 150 ºC. A further stress relaxation of up to 30 % occurs in the first 20 days after welding. Localised stresses are therefore unlikely to exceed 50 MPa when the canister is placed into storage. No negative effects have been observed in connection with this stress relaxation process.

In the storage period, which is indefinite, the canister is required to survive for several hundred thousand years. The canister outer temperature is expected to be close to 100 ºC for 100 to 200 years. During storage, repository processes will cause deformation and the generation of further localised stresses in the copper shell. The precise strains and related stresses which will arise are not well defined. The rate of development of these strains however, are such that the localised stresses in the copper shell are unlikely to increase above the levels present at the end of the holding period.

The Frost and Ashby deformation diagram referred to above defines a boundary at 100 MPa stress, below which deformation at the relevant temperatures is described as power law creep and above which it is described as power law breakdown creep. Processes which predominate in each stress regime are identified and the boundary is defined as the locus of points where the two processes on either side of the boundary are equally important. All the work reported is qualitatively consistent with the Frost and Ashby description.

It is also consistent with a model where at low stresses in the power law regime, failure occurs by the development and growth of cavities or cracks in grain boundaries. This provides a low strain to fracture failure. Increasing stress in the power law regime leads to a reduced level of intergranular cracking. Failure strains therefore increase with increasing stress. At the boundary between power law and power law breakdown, the brittle grain boundary cracking processes have equal importance with processes which favour the development of transgranular cracks. Above the boundary transgranular cracking processes dominate.

Results for tests on OF material indicate that the fracture strain at the boundary is approximately 10 % and at lower stresses it falls to less than 5 %. When sulphur is present in amounts exceeding 6 ppm fracture strains in the power law regime fall dramatically, in many cases to less than 1 %. This is attributed to the very low solubility of sulphur in copper which leads to segregation of sulphur to grain boundaries. As stresses are increased above the power law boundary, grain boundary cracking becomes less important and the effect of sulphur is no longer observed. In view of the low fracture strains observed for OF material in the relevant power law regime it is regarded as unsuitable for use in the copper shell.

OFP has been suggested as a satisfactory alternative to OF material for the copper shell. A small number of tests in the power law breakdown regime have indicated that failure strains in this regime may be adequate.

Creep strain rates for OFP in the power law breakdown regime are two orders of magnitude slower than rates predicted by the Frost and Ashby model for corresponding test conditions. Creep strain rates for OF material are in good agreement with the Frost and Ashby model over a wide range of temperatures and stresses in the power law and power law breakdown regimes. No tests have been conducted on OFP material in the power law regime at relevant temperatures because the slower strain rates observed are said to lead to tests which take too long. Tests in the power law regime at higher temperatures, 300 ºC plus, show clear evidence of cavity formation in grain boundaries but high failure strains. It is suggested by the writer that the high failure strains for these cases may arise as a result of processes which would not be available at lower temperatures and that satisfactory fracture strains may not be achieved in OFP material under relevant conditions. Further testing is required to determine properties in the power law regime.

1. Introduction

It is planned that spent nuclear fuel from the Swedish nuclear power industry will be disposed of by encapsulation in a copper canister which will be placed at a depth of 500 metres in granitic rock.

The insert of the disposal vessel is of cast iron and it is designed to withstand the external forces in the repository and any internal forces arising within the canister. The outer skin, is a copper shell which is 50 mm thick and it is designed to present a corrosion barrier to protect the insert.

The insert and the copper shell acting together provide a radiation barrier with regard to the contents of the canister.

The outer dimensions of the copper shell are roughly 1 m, diameter and 5 m. tall. The design provides for a 2 mm gap all round between the inner and outer vessels to aid assembly.

The copper shell will be fabricated from a copper tube to which forged and machined lids and bottoms are welded. The welding process will be either electron beam welding or friction stir welding.

It is important that the integrity of the copper shell is maintained for some hundreds of thousands of years and among other things it must be able to resist creep failure under the influence of residual manufacturing stresses and stresses which will arise in the repository.

The grades of copper which have been considered for the shell are Oxygen free high conductivity copper (OFHC) which will be referred to in this report as OF, and an OF copper to which 50 ppm of phosphorus has been added. The latter material will be referred to in this report as OFP. The reason for the choice of OF is its high thermodynamic stability and the addition of 50 ppm of phosphorus is made to improve creep performance.

Experiments on the two materials have been conducted over the past fourteen years and this report is a critical review of the information which has been made available to date.

Section 2 presents a brief review of knowledge on the creep processes in copper so far as they are important to the overall report. Section 3 presents information on the temperature and stress environments which will be experienced by the canister. The stress information is supported by a detailed review of relevant literature in appendix A. The main review and comments on the literature is in section 3 and conclusions appear in section 4.

2. Creep in copper

Creep processes which occur in a wide range of materials were described by Frost and Ashby (1982). They pointed out that creep is usually only important at temperatures exceeding 0.4 Tm for alloys and 0.3 Tm for pure metals where Tm is the melting temperature in degrees Kelvin. 0.3 Tm for copper is 134 ºC. Henderson (1994) pointed out that the 0.4 Tm rule for alloys is usually applied for engineering structures which are lifed at 30 years. The copper shell is made from an almost pure copper and the normally accepted lower temperature for creep might therefore be expected to be 134 ºC (0.3 Tm) for lives of 30 years. However as Henderson (1994) pointed out creep is a thermally activated process and the timescales involved in the service of the canister are so extreme that the possibilities of creep failure cannot be neglected. She went on to describe the creep processes as follows.

Classical creep occurs in three stages. Primary creep which occurs during and immediately after loading involves some work hardening and an increase in dislocation density. Secondary or steady state creep occurs through the major part of the component life, during this stage work hardening and recovery rates are more or less in balance and the dislocation density remains essentially constant. An increase in deformation rate known as tertiary creep usually precedes failure.

In normal engineering service primary creep is negligible, failure is not expected and therefore it is the secondary or steady state creep characteristics that are the basis of design practice.

The secondary creep rate $d\varepsilon/dt$ is given by the Norton-Bailey relationship,

$$d\varepsilon/dt=A\,\sigma^n e^{-Q/RT} \qquad (1)$$

where the symbols have their usual meanings and the stress exponent n may vary from 1 to 7 depending on the creep mechanism in operation. Usually the activation energy Q is the energy for self-diffusion. For constant temperature tests the equation is sometimes simplified to

$$d\varepsilon/dt=B\sigma^n$$

Three types of behaviour in secondary creep are identified by Henderson according to the stress regime, in the first, Harper and Dorn creep, which is diffusion controlled and occurs at low stresses and temperatures, the stress exponent n is 1. This creep mechanism is influenced by grain size and a small grain size increases creep rate. At intermediate stresses creep is controlled by dislocation flow and climb but climb is the rate-controlling factor. The stress exponent n for this mechanism of control may increase in the range 2 to 7 as stress increases. At very high stresses dislocation glide dominates and the power law behaviour breaks down. This stress condition induces the third type of behaviour which is referred to as power law breakdown and although stress exponents greater than 7 have been quoted for this stage, it is no longer described by the power law and the change in creep rate with increasing stress is more accurately described by an exponential relationship. All the work published in connection with the copper shell has been conducted in the medium or higher stress regimes where the stress exponent has been greater than 1.

Pettersson (2002) has suggested that at the low stresses and temperatures which he expects to arise on the copper canister in service, Coble or Nabarro–Herring creep might dominate. In both these mechanisms creep strain rate is proportional to stress as it is in Harper-Dorn creep.

All three mechanisms, Harper-Dorn, Nabarro-Herring and Coble creep are diffusion controlled. In diffusional creep vacancies generated close to grain boundaries normal to the applied stress migrate to grain boundaries parallel to the applied stress where they are absorbed. This process is akin to plastic deformation in that it provides a change in shape but it does not involve dislocation flow (as the higher stress processes do). The differences in the three types of process are in the diffusion mechanisms. Harper-Dorn involves diffusion of vacancies from the edges of dislocations normal to the tensile axis to the edges of dislocations parallel to the tensile axis. At higher temperatures the process occurs through the bulk of the grain (H-D creep) whilst at lower temperatures it occurs along the cores of the dislocation network (H-DP), a form of pipe diffusion. Nabarro-Herring creep is a higher temperature process which depends on bulk diffusion of vacancies whilst Coble creep, which occurs at lower temperatures depends on vacancy diffusion along grain boundaries (Nabarro (2002)). Creep rates are reported to be inversely proportional to grain size for H-D creep or H-DP (Henderson 1994), whilst Nabarro (2002) reports that they are inversely proportional to square of grain size for Nabarro-Herring creep and inversely proportional to cube of grain size for Coble creep.

Whilst the differences between the several diffusional creep mechanisms may be subtle they are all substantially different from the mechanisms involving flow which occur at higher temperatures and stresses. Extrapolation of results from tests carried out where one type of deformation mechanism is dominant into a service regime where the other type of mechanism is dominant is clearly of very dubious value. The Pettersson view that the most likely mechanism for creep in service is Coble creep must therefore be treated seriously as all the test used to qualify the canister for service have been conducted at high stresses for short times where the deformation process has been dominated by dislocation flow.

The deformation mechanism map for pure copper with a grain size of 100 μm, Figure 1, (overleaf) is taken from Frost and Ashby (1982). The contours on the map correspond to constant shear strain rates $d\chi/dt$ and the areas of predominance of the different deformation mechanisms are shown. This map has been referred to and used by most workers involved in the canister for the Swedish Nuclear waste disposal programme.

The vertical axis corresponds to the applied shear stress and this may be converted to tensile stress for the simple case through the relationship.

$$\sigma_t=3^{1/2}\sigma_s \qquad (2)$$

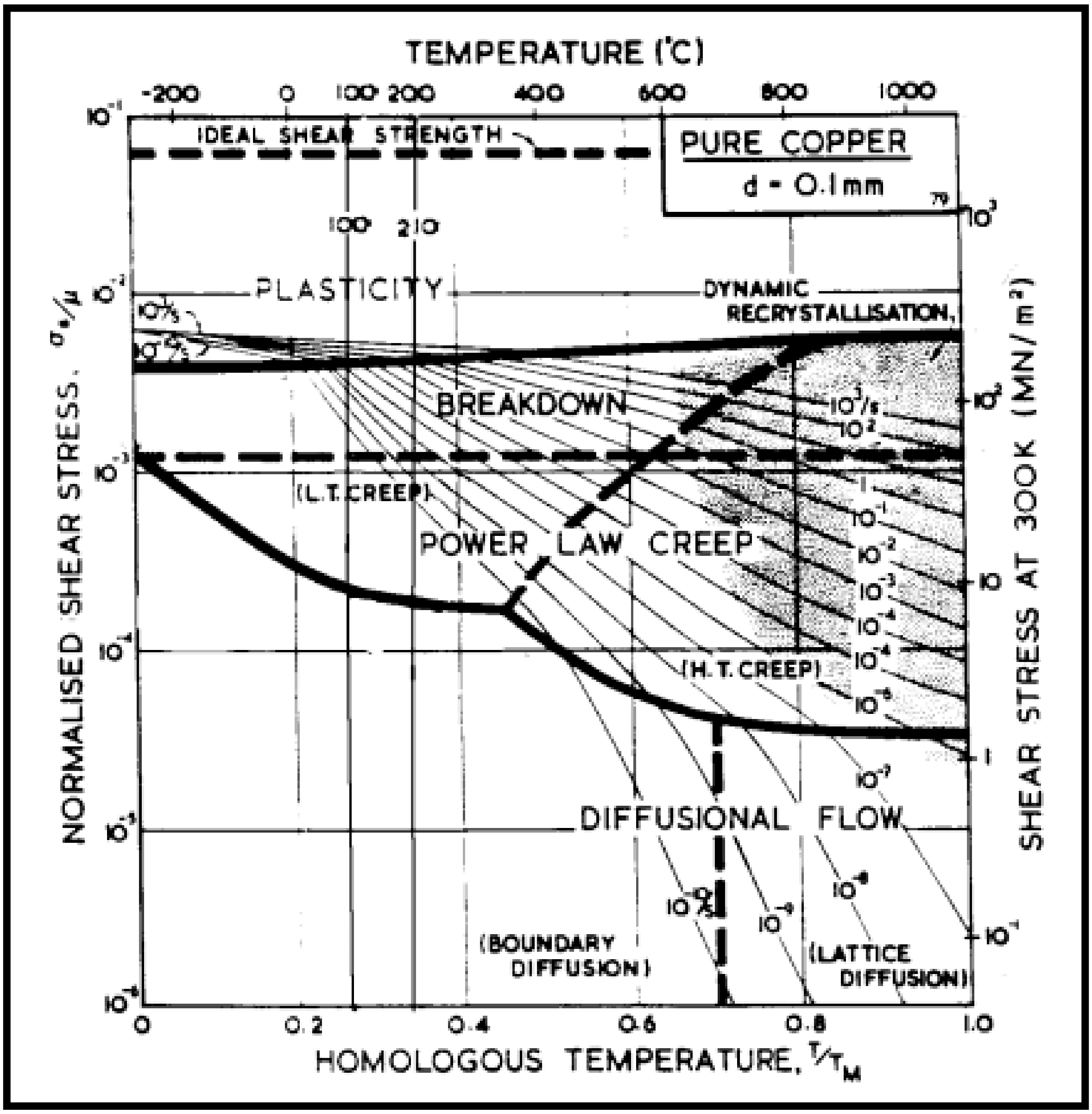

Figure 1. Deformation diagram for pure copper (after Frost and Ashby-1992)

Using this relationship and the deformation map the boundary between power law and power law breakdown behaviour is calculated to be at approximately 100 MPa and to be essentially independent of temperature. Similarly the boundary between power law and diffusional flow at 100 ºC is calculated to be at about 17 MPa, whilst a load of 50 MPa at 100 ºC is in the middle of the power law behaviour regime.

It is very important to recognise that the regions defined by the boundaries of the map are areas of predominance of the deformation mechanisms involved in secondary creep. The overall model is one in which a number of deformation mechanisms are available to the polycrystal and the rate of each one responds differently to changes in conditions of temperature and stress and possibly to metallurgical condition. Thus several mechanisms may operate simultaneously depending on applied stress and service temperature. The boundaries on the map define the locus of points at which two mechanisms are equally important. A single mechanism will dominate when conditions are well away from any boundary (Frost and Ashby 1982).

It is helpful to understand how deformation maps are derived. They were developed by Frost and Ashby for many materials by using a combination of theoretical analysis and experimental measurements. Where possible established values for parameters in the equations describing deformation processes were employed to define the general shape of the relationships between strain rate and temperature. Line fitting to experimental results was then used to establish useful values for the unknown parameters. The parameters so derived were then used together with the established parameters to complete the map by extrapolation from the published experimental data. Frost and Ashby used data from 29 works published in the period 1951 to 1968 to construct the map for copper (figure 1). They make it very clear that the map defines only the modes of deformation and strain rates in secondary creep. They are not relevant to creep lives because fracture strain is not defined. They also stress that creep does not stop when power law behaviour is suppressed, that is at stresses in the diffusional flow regime.

Examination of the experimental data used by Frost and Ashby reveals that varying states of cold work and presumably (although not specifically stated) varying states of purity of the experimental materials as well results from tension, torsion and compression testing were employed. This suggests that initial dislocation density and low levels of impurities and mode of stressing have little effect on the secondary creep behaviour of almost pure copper.

A very interesting observation from the map is the apparently strong sensitivity of the mechanism involved in change over from power law behaviour to power law breakdown behaviour to stress, coupled with a relative lack of sensitivity to temperature. The stress level involved is approximately 100 MPa tensile. Frost and Ashby define power law behaviour as steady rate flow, with an implication of some work hardening. They define power law breakdown as flow at constant structure, that is such that recovery occurs at the same rate as work hardening.

With this picture of the creep behaviour of almost pure copper it is possible to estimate the minimum creep rates for OF copper at stresses which correspond to the boundaries where dominance of any particular creep mechanism changes. Thus at 100 ºC the boundary between diffusional creep and power law creep occurs at approximately 17 MPa (tensile). For this stress the secondary creep rate is less than the minimum rate of 10^{-10} sec^{-1} considered by the diagram. Extrapolation suggests however that for this stress the creep rate is no more than 10^{-15} sec^{-1}. The time for 1 % strain by these mechanisms would therefore be of order one million years. The boundary between power law and power law breakdown behaviour arises at approximately 100 MPa and at 100 ºC the corresponding creep rate would be of order 10^{-11} to 10^{-12} sec^{-1}. At these rates the time for 1 % strain would be between 100 and 1000 years. All the published work for OF and OFP coppers connected to the copper canister programme have been conducted in the power law or power law breakdown regimes. In the main temperatures exceeding 100 ºC have been used in order to accelerate the tests.

3. Creep in the copper shell

3.1 Service conditions

3.1.1 Time

The service life of the copper–iron canister may be divided into two main components. The first is the period between welding of the lid and emplacement which is termed the holding period. According to Josefson et al (1993) this may be from a few days to one year. The second component is the period after emplacement in the repository and in this stage the canister is required to survive for more than 100,000 years (Nilsson 1992, Werme 1998)

3.1.2 Temperature

Josefson et al (1993) states that, after welding of the lids to the canister, heat generation by the welding and the fuel will raise the outside temperature of the canister to 100-150 ºC and that this will gradually decrease during the holding period. After emplacement in the repository the temperature is expected to be approximately 100 ºC for 100 to 200 years (Henderson et al 1992, Werme 1998).

3.1.3 Stress

3.1.3.1 Residual stresses from manufacturing

Residual stresses from manufacturing are discussed in Appendix A with the following conclusions;

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1. Welding and stress redistributions which occur in the holding period will cause local strains, which could in the worst case be as high as 14 %.
2. Owing to dynamic recovery during and immediately after welding and the high temperature in the immediate post welding period, stresses arising from the welding strains will be relaxed rapidly to levels which correspond to 0.1 % strain at the ruling temperature (this is approximately 75 MPa at 100 ºC or 50 MPa at 150 ºC).
3. A further 30 % stress relaxation will occur during the first 20 days after welding the lid and the relaxation after this time will continue at a reducing rate with time. It is to be expected therefore that the peak localised internal stress at the time of placing in the repository will be close to 50 MPa.
4. The location of the peak strains will be close to the lid corner on the inside of the copper shell.

3.3.1.2 Stresses arising in the repository

Stresses arising in the repository are discussed in detail in appendix A. The conclusions are as follows;

5. The uniform pressures which might arise from ideal bentonite swelling, hydrostatic pressure and the ice load should not cause a creep problem by virtue of the fact that they are hydrostatic.
6. Collapse of the overpack onto the liner will lead to localised stress concentrations but their rate of development will be such that the levels of localised stresses present at deposition will not be exceeded.
7. Non-uniform swelling of bentonite can lead to localised stress concentrations but their levels will not exceed those of the stress concentrations present at the time of deposition. Peak localised stresses should not therefore exceed 50 MPa.
8. During long-term creep in the repository the dominant creep mechanism power law creep with activation energy of 197 kJ/mol. In this stage the creep mechanism is dislocation glide with vacancy assisted climb as the rate controlling step.
9. In the very long term when stresses and temperatures both decline the creep mechanism is likely *to involve* diffusional *flow*.

3.2 Materials and testing

3.2.1 Oxygen Free Copper (Cu-OF)

Most of the published work connected with the copper-iron canister programme has been conducted on two materials Cu-OF and Cu-OFP. Parameters measured have been creep ductility (strain to failure) and stress exponent in secondary creep (see equation 1). The reason for the ductility measurement is the importance of ductility to the serviceability of the canister and the importance of stress exponent is its utility in extrapolating behaviour to longer times at lower temperatures and stresses. A secondary use of the stress exponent is as an indicator of the dominant deformation process under the test conditions (see section 2). Some of the published work also includes fractography studies in varying levels of detail.

Henderson et al (1992) and Henderson (1994) presented results of work on OF copper compared with the published results of four other workers. All used OF copper, the grain size range varied from 25 µm to 250 µm. The test temperatures varied from 75 ºC to 450 ºC and test stresses varied from 20 to 170 MPa. A total of twelve sets of results were plotted on a graph of $d\varepsilon/dt$ (min) versus log stress. The slope of this graph is therefore the stress exponent in the Norton-Bailey relationship. Five of the twelve plots showed a change of slope from less than 7 to substantially more than 7 occurring in the stress interval from 80 MPa to 100 MPa. All remaining results were for tests at stress levels below 100 MPa and they all had stress exponents between 4 and 5. The Henderson work included tests in both the power law and the power law breakdown regimes. On the basis of this body of evidence the deformation plot (Figure 1) appears reliably to predict the transition from power law to power law breakdown behaviour for OF copper. This is reinforced by later work (Henderson and Sandström 1998) in which strain rates in tests on the same material tested at stress values below 100 MPa yielded a stress exponent of 4 whilst tests using stresses exceeding 100 MPa yielded stress exponents of more than 10.

The same work, by Henderson et al (1992, 1994, 1996 and 1998), presented results indicating that failure strains for OF material tested in the power law break down regime were in the range 10 % to 50 % whilst the same material tested in the power law regime had failure strains of less than 10 %. Failures in the power law regime were intergranular whilst failures in the power law breakdown regime were transgranular. In the power law breakdown regime where failure strains were generally high there was a clear trend towards reducing failure strain with reducing stress. In the power law regime almost all specimens failed at 1 % strain or less.

A further observation was that the activation energy for steady state creep at stresses below 100 MPa was 197 kJ/mole which is equal to the energy for self-diffusion in copper whilst the activation energy for steady state creep at stresses exceeding 100 MPa had no physical significance. This suggests that the power law creep behaviour is diffusion controlled whilst the power law breakdown behaviour is not diffusion controlled.

Metallography on failed specimens in this work revealed that a specimen tested at 45 MPa had grain boundary cracks and cavities along the entire gauge length whilst in a specimen tested at 85 MPa had fewer cracks and cavities and they were located close to the final fracture (Henderson and Sandström 1998 and Forsberg 1994).

The observations fit a behaviour model in which the primary deformation mode at low stresses leads to the development of cracks and cavities in grain boundaries. At higher stresses, plastic flow occurs, the development of intergranular cracks is inhibited and failure is dominated by the development of transgranular cracks. The stress at which the latter mechanism dominates is the transition from power law to power law breakdown behaviour. Similarly in the power law breakdown regime a marked increase in fracture strain with increasing stress is consistent with increasing inhibition of crack formation and growth as plastic processes become increasingly dominant. This is also consistent with the Frost and Ashby prediction that at the power law breakdown boundary in Figure 1 the two deformation processes are equally dominant whilst for a stress well below the boundary, power law behaviour (intergranular cracking) is clearly dominant.

The deformation map is prepared for pure copper with a grain size of 100 µm. No general information is available on the effects of grain size or low levels of impurities but the results of this early work suggest the transition from power law to power law breakdown behaviour has a low sensitivity to both.

In view of the residual stresses arising in manufacture and the additional localised stresses arising in storage, the brittle behaviour exhibited by OF copper in the power law regime render it unsuitable for use in the copper–iron canister.

3.2.2 Effects of Sulphur

The Henderson work (Henderson et al 1992, 1994, 1996 and 1998, and Forsberg 1994) compared the creep properties of OF material, with 6 ppm sulphur content and with OF material having a 10 ppm sulphur content. The 10 ppm material was fine grained forged bar and the 6 ppm material was fine grained extruded bar. In two sets of specimens containing 10 ppm sulphur tested at stresses of 100 MPa or higher, fracture strains varied from 50 % at the highest stresses to 10 % at the lower stresses. One set of specimens was tested at stresses from 80 MPa to 120 MPa. The ones tested above 100 MPa gave failure strains exceeding 10 % whilst the ones below gave failure strains of 5 %. A final set of eight specimens, all tested at 80 MPa or less all failed at less than 1 % strain by the intergranular route. Only three specimens of 6 ppm material were tested to failure. They were all tested at stresses less than 100 MPa and they all failed at close to 10 % strain. These results suggest that for fine grained OF copper;

1. Creep fracture strains decrease from 50 % high in the power law breakdown regime, to 10 % at the power law/power law breakdown boundary and this is not influenced by 10 ppm of sulphur.
2. For material containing 10 ppm sulphur tested well in the power law regime failure strains fall to less than 1 %.
3. The very rapid decrease in ductility with decreasing stress which occurs in material containing 10 ppm sulphur is not observed as test stress is reduced in the range below 100 MPa when sulphur content is 6 ppm.
4. It appears that the presence of sulphur contents exceeding 6 ppm is responsible for the rapid reduction in ductility from 10 % to 1 % which occurs when power law behaviour becomes increasingly dominant.

1 and 3 above are consistent with the behaviour model described earlier for OF copper. At low stresses grain boundary cracking dominates the creep fracture mode, as stresses are increased plastic processes lead *to inhibition of grain boundary cracking* and increased fractures strain. At around 100 MPa the plastic processes start to control the fracture process and grain boundary cracking has less significance as stresses are further increased.

The onset and eventual dominance of plastic processes should lead to increased necking as test stresses are increased. This would have a disproportionate and misleading effect on the improvement of measured fracture strain with increasing stress. Unfortunately no comments are made on the effects of necking. It is highly likely however that when fracture strains of order 50 % are measured a high proportion of that strain is localised in the neck. If the conventional view that failure occurs at the onset of necking is adopted then failure strains would be much lower.

The presence of 10 ppm sulphur has a disastrous effect on failure strain when tests are carried out in the power law regime. It is suggested (Henderson et al 1992 and Henderson 1994, Forsberg 1994) that this is due to a reduction in the surface energy of grain boundary cavities and cracks caused by segregation of sulphur to grain boundaries. Very good fractographic evidence is provided by Henderson et al (Henderson et al 1994 and 1998) in support of this argument. Henderson discusses sulphur solubility in copper and points out that at 100 ºC the solubility is less than 4 ppm, this leaves at least 2 ppm to segregate to grain boundaries from the 6 ppm material and 6 ppm from the 10 ppm material. The concentrations arising in grain boundaries will depend on the excess present over the solubility limit and the grain size.

Sulphur segregation does not influence failure when power law breakdown occurs because failure is then transgranular.

Forsberg (1994) reported Scanning electron microscope (SEM) and microanalytical transmission electron microscopical (ATEM) studies on fracture surfaces of the 6 ppm and 10 ppm sulphur specimens referred to above. Segregation of sulphur to grain boundaries was observed on creep tested specimens of OF and OFP material containing 6 ppm sulphur as well as on material containing 10 ppm sulphur. However when 10 ppm sulphur was present the concentrations of sulphur in grain boundary cavities was higher.

Forsberg (1994) quoted limited creep test results and speculated on the influences which sulphur and phosphorus might have on creep properties. He asserted that phosphorus increases creep ductility in OF copper and that poor ductility may arise from a large grain size and or a lack of control of sulphur content. He referred to the tests on OF material at 180 ºC (Henderson 1994) which failed at strains of less than 10 %. These failures were intergranular and were associated with cavitation in the grain boundaries. Material having a sulphur content of 10 ppm and a grain size of 370 µm failed at 1 % strain whilst material having 6 ppm sulphur and a grain size of 45 µm failed at close to 10 % strain. Forsberg attributed all the low strain to fracture failures observed on these specimens to the effects of sulphur and did not point out that all the tests considered were in the power law regime. The work described above for OF copper indicates that low strain to fracture failures (in the region 10 % or less) are to be expected in the power law regime when, *and probably because*, behaviour is dominated by intergranular cavitation and cracking. This is irrespective of sulphur content. The very low fracture strains (of order 1 %) observed are accurately attributed to higher sulphur content (10 ppm) and coarser grain size as discussed by Henderson (1994).

Andersson et al (1999) reported that increases in sulphur content from 6 ppm to 12 ppm had no effect on creep properties. This conflicts with the observations and arguments presented above. The reason for Anderssons observation was that all his tests on these materials were carried out high in the power law breakdown regime where grain boundary failure does not occur and failure strain is therefore not sensitive to sulphur content.

3.2.3 Effect of 50 ppm phosphorus additions (Cu-OFP)

3.2.3.1 Solubility

Henderson (1994) considers the solubility of phosphorus and points out that 50 ppm is well below the solubility limit in the temperatures of interest but that some segregation to grain boundaries might occur. Forsberg (1994) was able to observe segregation of sulphur in material containing 6 ppm but he failed to observe any evidence of segregation of phosphorus when it was present at the 50 ppm level. There is no evidence to support assertions by Forsberg 1994 and Henderson et al 1992 and Henderson 1994 that co-segregation of sulphur and phosphorus might limit the embrittling effects of sulphur.

3.2.3.2 Effect on creep rates

Henderson (1994) states that addition of 50 ppm phosphorus to Cu-OF causes a reduction in creep rate of two orders of magnitude.

This conclusion is based on consideration of results of one OF specimen and one OFP specimen. The test conditions for the two specimens were 215 ºC and 100 MPa. The measured minimum strain rates were $5.5*10^{-8}$ for the OF specimen and $5.9*10^{-10}$ for the OFP specimen. The difference is indeed two orders of magnitude as claimed. It is misleading however to suggest that this result for two specimens represents a general case. The test stress for the particular set of results used was on, or close to, the boundary between power law and power law breakdown behaviour for both specimens, and all the theoretical and experimental studies have agreed that the stress exponent increases as the transition from power law to power law breakdown behaviour occurs. Thus the slopes of the trend lines linking log dε/dt to log stress change at the transition stress. The slope of the trend lines at higher stresses is higher than the slope of the trend lines at lower stresses and the two trend lines for a specific material cross at the transition stress. The actual slopes on either side of the transition depend on test temperature and on the chemistry of the material. There is no evidence to suggest that the magnitude of the change in slope at the boundary of power law and power law breakdown behaviour is constant with changes in temperature or with changes in composition. Thus whilst a two order of magnitude difference in the creep rates of the two specimens was observed at a particular stress, there is nothing in this work to suggest that the difference in creep rates of the materials which they represent would be the same at any other stress.

Pettersson (2002) has looked more closely at the Henderson (1994) results and plotted the pooled data for OF and OFP specimens tested at 215 ºC on a plot of log dε/dt versus test stress. He concludes that a factor of 10 is a better estimate of the effect of phosphorus on minimum creep rates at the transition stress. His plot also demonstrates the danger inherent in extrapolating data across boundaries where mechanisms change. For this case extrapolating the data for OF material to higher stresses leads to the absurd suggestions that for stresses higher than 140 MPa OF material has a lower minimum creep rate than OFP material and for stresses in the region of 50 MPa the OFP material would have a creep rate which is five to six orders of magnitude lower than that of OF material.

A further area for concern in the comparison of these minimum creep rates arises from consideration of failure strains. All but three of the OF specimens considered by Henderson (1994) contained 10 ppm sulphur and failed at strains of less than 1 % whilst all the OFP specimens contained 6 ppm sulphur and they failed at strains exceeding 30 %. In view of the very low fracture strains observed it is questionable whether or not a true minimum creep rate was achieved in the OF specimens. Interestingly the three

OF specimens which contained only 6 ppm sulphur failed at higher fracture strains (circa 10 %) even though they were tested in the power law regime and failed by intergranular cracking. These specimens had comparable minimum creep rates to the higher sulphur specimens even though their fracture strains were so much higher, this is not explained.

Forsberg (1994) compares the results from single tests at 100 MPa on OF and OFP material, the former test was at 215 ºC whilst the latter was at 300 ºC. They had almost identical creep lives of 200 to 300 hours but the OF material failed at 10 % strain whilst the OFP material failed at 40 % strain (of which 15 % was in the neck). Details of the fracture modes are not given but the bare result suggests that presence of phosphorus and /or the increase in test temperature has caused an increase in ductility in the OFP material over that observed in the OF material. The strain rate in the OFP material was 10 times higher than it was in the OF material whilst figure 1 indicates that, in the absence of a difference in composition, the difference in temperature of the two tests should have led to a one hundred fold increase in strain rate. This suggests that an increase in resistance to deformation has in fact been provided by the phosphorus.

Both the above examples suggest that, despite misgivings concerning comparisons between single specimens or tests made under different conditions, addition of 50 ppm of phosphorus leads to a reduction in minimum creep rate at the transition stress of between one and two orders of magnitude. Standing alone they do not provide conclusive proof or any indication of what the differences in minimum creep rate might be at lower stresses. The latter example suggests that the presence of phosphorus may also lead to an increase in ductility. This conclusion must also be approached with caution because the test temperature of 300 ºC may have contributed to the effect.

3.2.3.3 Effects on fracture strain

As well as creep rate, fracture strain is important to creep life. In OF material a progressive reduction in fracture strain occurs as creep stress is reduced from high in the power law breakdown regime to low levels of stress in the power law regime (Henderson and Sandström 1998).

The Henderson 1994 paper quotes results for failure strains of OF material in the power law breakdown regime and the values of failure strains were in the same range as the tests on OFP material, 30 % to 60 %. Henderson and Sandström (1998) also provides a plot of log creep rate x lifetime versus log rupture strain for OF material. This shows failure strains up to 50 %. These results indicate that fracture strains of the two materials may be similar in the power law breakdown regime. The comparison suggests that any difference could be a result of increased necking or slightly higher plasticity in the case of the OFP material. This could be a result of testing at higher temperatures.

Forsberg (1994) reported test results obtained by others (and also referred to by Henderson (1994)) on OFP material. He did not give test conditions but examination of his source material reveals that they were in the power law breakdown regime. He reported failure strains of 30 % to 40 % as increases in ductility brought about by the presence of phosphorus. Consideration of the data for OF material tested in the power law breakdown regime (and referred to above) indicates that the differences in the observations on the two materials were small when compared on a like for like basis (Henderson 1994).

Henderson (1994) showed a clear trend of reducing fracture strain with reducing stress exponent (and therefore stress) for OFP material. Her results were all in the power law breakdown regime but there is nothing to suggest that that trend will not continue as stress is reduced in the power law regime as it does for OF copper. The main factor controlling failure strain was test stress. Specimens of OFP material tested at the same stress as the OF specimens referred to above had slightly higher failure strains and this may be accounted for by the higher temperature of the tests.

3.2.4 Combined effects of sulphur and phosphorus.

Forsberg (1994) suggested that the segregation of sulphur which “probably” causes the critical intergranular fracture in OF material is delayed in the presence of phosphorus and that this may give OFP material a longer lifetime than OF material. He concluded that this was not the case. He did not however explain differences in fracture strain between phosphorus bearing and nominally phosphorus free materials. This was an early work. With the benefit of observations over a longer timescale, and reported in earlier sections of this report, it is possible to explain his observations in the following way. His OF observations were in the power law regime on material with 6 ppm sulphur. This material tested under these conditions failed at a fracture strain of 10 %. This is typical of a low sulphur material under these test conditions. The apparently low fracture strain is a consequence of intergranular failure which may or may not have been influenced by the low sulphur content. The OFP material referred to was all tested in the power law breakdown regime where the low strain grain boundary failures are not observed irrespective of sulphur or phosphorus contents. The search for combined effects of sulphur and phosphorus under these conditions was therefore futile. Any combined effects would only be apparent in the power law regime and if they were observed they would be important. No tests were conducted in this regime.

3.2.5 Effects of grain size

Henderson (1994) predicted that if the embrittlement which is attributed to sulphur in the power law regime depends on the segregation of sulphur to grain boundaries, then the critical sulphur level would depend on grain size. This implies that coarser grained material would be susceptible to sulphur embrittlement at lower sulphur levels than fine grained material. Andersson (1999) investigated the effect of grain size. All his tests were high in the power law breakdown regime and no effects of grain size were detected.

3.2.6 Attempts to test OFP in the power law regime

Henderson et al (1992 and 1994) reports 9 results from tests on CuOFP. Eight of the nine tests were carried out at stresses exceeding 100 MPa and the stress exponents were well in excess of 7. Fracture strains were in the range 30 % to 45 % and a substantial part of this (up to15 %) was in the neck (Forsberg 1994). The tests were clearly carried out in the power law breakdown regime.

These results emphasise the problems associated with obtaining useful information in limited timescales. It is necessary to work at stresses well below 100 MPa to avoid power law breakdown behaviour. This is not difficult with the high sulphur OF copper containing 10 ppm sulphur because fracture strains are so low. Typical creep rates are 10^{-9} to 10^{-10} seconds^{-1} and failure strains are 1 %. With OFP material (which contains only 6 % sulphur) fracture strains tend to be higher at up to 50 %. Therefore secondary creep rates of 10^{-8} to 10^{-9} seconds^{-1} are required to achieve failure in the same test time. Unfortunately the higher stresses which are required for this creep rate place the OFP tests in the power law breakdown regime (100-160 MPa).

Henderson (1994) reports tests on OFP at 300 ºC and 350 ºC which have clearly been aimed at achieving power law behaviour in acceptable timescales. The number of tests is not disclosed but is said to be limited. Stress exponents suggest that power law behaviour was achieved. Failure strains were in the range 20 % to 45 % however. These are significantly higher than the 10-12 % failure strains reported for tests on OF material (containing 6 ppm sulphur) in the power law regime and very much higher than the 1 % maximum fracture strain recorded in tests on OF material containing 10 ppm sulphur in the power law regime.

The deformation mechanism in all these power law regime tests is expected to be dislocation flow and the rate controlling process is expected to be dislocation climb (see section 2). There is nothing in the published information to suggest that this may not have been so. Fracture mechanisms do vary between the different tests however. It is clear from a consideration of all the information that there is a consistent trend away from failure by intergranular cracking towards failure by transgranular cracking for both OF materials (6 ppm and 10 ppm sulphur) as test stress is increased through the power law regime and into the power law breakdown regime. It is also clear that the change in fracture mode occurs at higher stresses for the higher sulphur bearing material. This trend is not quite so clear for the OFP material, possibly because so few tests have been completed in the power law regime and the ones which have been completed, have been at relatively high temperatures compared with all other tests. The observations made on these specimens are that creep rates are high (10^{-7} seconds^{-1}), the failures are ductile and large dimples are present in the fracture surfaces. It is possible that these dimples arise from grain boundary cavities which, at lower test temperatures would have led to intergranular failure, but it is by no means demonstrated. It is therefore uncertain whether the higher test temperature or the presence of phosphorus is responsible for the higher ductility observed in the OFP tests in the power law regime.

A single test on OFP at 30 MPa was carried out at 450 ºC (Henderson 1992), the secondary creep rate for this test at $2.5*10^{-7}$ is ten times higher than the value for pure copper predicted by figure 1. This test fell in the high temperature creep zone of the power law regime. The creep life was very short at 195 hours. It gave a high strain to fracture, 32 %, and it is reported that the fracture surface contained large dimples which were sulphur rich. The presence of sulphur in the dimples suggests that they originate from intergranular cavities but the high fracture strain suggests that these cavities may have contributed to but were not responsible for the failure. This may be explained by the increased plasticity which was promoted by the very high temperature of this test and it may well be an extension of the behaviour observed in the tests at 300 ºC to 350 ºC referred to above.

The significance of the above fractographic information is that it demonstrates that the grain boundary cavitation was occurring under those test conditions. It has to be assumed therefore that, either the cavitation process also occurs at lower temperatures where the plastic processes which have dominated fracture behaviour in the higher temperature tests do not operate, or that phosphorus has the effect of preventing cavitation in grain boundaries and this effect is neutralised by increases in temperature.

If the former is true, then low stress brittle failure of OFP is a possibility. If the latter is true it is necessary to propose a mechanism for inhibition of cavity formation involving phosphorus. As all attempts to detect evidence of segregation of phosphorus to grain boundaries have failed, the former explanation is favoured at present.

3.3 Comparison of experimental data with theoretical predictions.

Whilst the discussion in 3.2.3 above suggests that addition of 50 ppm phosphorus to OF material results in an increase in the force required for a given secondary creep rate, a direct comparison of the results to determine the effects of phosphorus has been difficult because only a single set of test conditions have been duplicated for the two material types. A comparison of secondary creep rates for all specimens from the two materials with the predictions for pure copper under the same conditions, taken from figure 1, could be more helpful however.

Individual minimum creep rate results have been compared with predictions of minimum creep rates for pure copper under the same conditions and the general trends with temperature and stress are in agreement with the theoretical trend for both material types. The general scatter of the experimental points about the theoretical prediction lines also appear similar for both material types.

Mean variations between experimental minimum creep rates for the two material types across the complete range of temperatures and stresses is not possible because insufficient data is available for OFP in the power law regime. However, Henderson 1994 and 1998 has provided plots of strain rate versus stress across the entire range of temperature and stress for OF material, and Henderson et al (1992 and 1994) has tabulated some results for OF and OFP material in the power law and power law breakdown regimes. Data has been extracted from the plots in the 1994 and 1998 works and used together with the tabulated data from 1992 to enable a comparison of secondary creep rates for OF and OFP materials against the predictions of Frost and Ashby (Figure 1) as a standard. In order to render the published data compatible with the Frost and Ashby map it has been necessary to convert tensile stresses and strain rates to shear stresses and strain rates and engineering shear stresses to true shear stresses.

For convenience predictions of the ratio between predicted and observed shear strain rates have first been made using the engineering shear stress values and these are given in columns 8 of tables 1 and 2 (overleaf). A correction factor has then been applied to this ratio to take account of the uniform reduction in area of the specimens. The correction factor for each specimen was calculated by reference to the simplified form of equation 1, referred to earlier and given below.

$$d\chi/dt = B\,\sigma^n$$

The required correction factor (f) on $d\chi/dt$ is therefore given by

$$f=(l_1/l_0)^n$$

where l_0 is the original specimen gauge length, l_1 is the gauge length at the minimum creep rate and n is the stress exponent in equation 1.

For all specimens which failed at fracture strains of 0.2 or less, zero necking has been assumed (this is generally a sound assumption as in most of these cases failure strains were less than 0.01) the gauge length at fracture for theses cases has been taken as l_1. The strain for minimum strain rate in specimens which strained by more than 20 % was taken as 0.2 which yields a value of 1.2 for l_1/l_o. This was in order to avoid large errors arising from necking which occurred in specimens exhibiting high failure strains (Forsberg 1994).

Stress exponents for the specimens were given in the relevant papers and are listed in columns 9 of tables 1 and 2. Correction factors (f) are given in columns 10 and the ratios of corrected predicted to actual shear strain rates are given for individual specimens in columns 11, the mean ratios for each specimen group are given in column 12.

In view of the uncertainty in extracting data from diagrams rather than the source and of the assumptions used the results in tables 1 and 2 should be regarded as best estimates. In spite of this caviat, it is clear that the predicted performance of the OF material is very close to the observed performance across the whole range of temperature and stress examined. The predicted strain rates for OF material are within one order of magnitude of the observed strain rates in 24 out of 27 cases which cover both the power law and power law breakdown regimes. It has to be concluded that the Frost and Ashby model gives a good representation of the behaviour of OF copper.

Only eight sets of data are available for OFP material and they are all at temperatures exceeding 200 ºC and in the power law breakdown regime. Nevertheless strain rates are consistently two orders of magnitude lower than predicted by the Frost and Ashby model. It does appear that the addition of 50 ppm phosphorus to the nominal OF composition has, in this very limited number of tests, led to a substantial increase in resistance to creep deformation. The magnitude of the effect is very surprising as a two order of magnitude increase in resistance to deformation in this temperature range corresponds to an approximate increase in shear stress for a shear strain rate of 10^7 sec^{-1} from 60 MPa to approximately 80 MPa. This effect is not understood and no reasonable explanation has been offered. There is nothing from the reported work which indicates that the same benefit of phosphorus will apply in the power law or diffusional flow regimes and in view of the changes in rate controlling processes in the different regimes it is not safe to assume that this benefit which has been observed in tests will also be available in the expected repository conditions.

Table 1. Comparisons of observed secondary creep rates in the power law breakdown regime for OF and OFP materials against predicts according Frost and Ashby (Figure 1)

Material	Test Temp ºC	Tensile Stress MPa	Minimum Strain rate $(d\varepsilon/dt)$	Shear Stress MPa	Shear Strain rate $(d\chi/dt)$	Predicted $d\chi/dt$ (P)	Predicted/ Observed $d\chi/dt$ (P/A)	Stress Exponent (n)	Correction Factor $(1+\varepsilon_f)^n$	Corrected P/A	Mean P/A
OF	75.00	160.00	2.50E-07	94.1	4.25E-07	5.00E-10	1.18E-03	2.70E+01	1.37E+02	1.62E-01	
	75.00	150.00	2.30E-08	88.2	3.91E-08	9.00E-11	2.30E-03	2.70E+01	1.37E+02	3.16E-01	
	75.00	140.00	1.00E-09	82.4	1.70E-09	8.00E-11	4.71E-02	2.70E+01	2.13E+01	1.00E+00	
	75.00	135.00	2.00E-09	79.4	3.40E-09	8.00E-11	2.35E-02	2.70E+01	1.37E+02	3.23E+00	
	75.00	100.00	6.00E-11	58.8	1.02E-10	5.00E-13	4.90E-03	2.70E+01	1.37E+02	6.73E-01	
											1.08
OF	145.00	120.00	1.00E-07	70.6	1.70E-07	1.00E-09	5.88E-03	1.00E+01	5.23E+00	3.08E-02	
	145.00	110.00	3.00E-08	64.7	5.10E-08	1.00E-09	1.96E-02	1.00E+01	4.68E+00	9.17E-02	
	145.00	100.00	1.00E-08	58.8	1.70E-08	6.00E-10	3.53E-02	1.00E+01	5.05E+00	1.78E-01	0.10
OFP	215.00	120.00	1.30E-08	70.6	2.21E-08	1.00E-07	4.52E+00	1.50E+01	1.54E+01	6.97E+01	
	215.00	140.00	6.20E-08	82.4	1.05E-07	6.00E-07	5.69E+00	1.50E+01	1.54E+01	8.77E+01	
	215.00	100.00	1.30E-09	58.8	2.21E-09	7.00E-08	3.17E+01	1.50E+01	1.54E+01	4.88E+02	
	215.00	160.00	8.50E-08	94.1	1.45E-07	1.00E-05	6.92E+01	1.50E+01	1.54E+01	1.07E+03	
	215.00	150.00	3.30E-07	88.2	5.61E-07	1.00E-06	1.78E+00	1.50E+01	1.54E+01	2.75E+01	347.82
	250.00	100.00	4.00E-09	58.8	6.80E-09	3.00E-07	4.41E+01	1.35E+01	1.28E+01	5.66E+02	566.00
	250.00	120.00	1.50E-07	70.6	2.55E-07	1.00E-06	3.92E+00	1.35E+01	1.28E+01	5.03E+01	
	300.00	100.00	2.80E-07	58.8	4.76E-07	4.00E-06	8.40E+00	6.70E+00	3.58E+00	3.01E+01	30.10

Table 2. Comparisons of observed secondary creep rates in the power law regime for OF materials against predictions according to Frost and Ashby (Figure 1)

Material	Test Temp ºC	Tensile Stress MPa	Minimum Strain rate $(d\varepsilon/dt)$	Shear Stress MPa	Shear Strain rate $(d\chi/dt)$	Predicted $d\chi/dt$ (P)	Predicted/ Observed $d\chi/dt$ (P/A)	Stress Exponent (n)	Correction Factor $(1+\varepsilon_f)^n$	Corrected P/A	Mean P/A
OF	145	80	2.00E-09	47.1	3.40E-09	1.00E-10	2.94E-02	5.00E+00	1.22E+00	3.59E-02	
11 ppm	145	70	8.00E-10	41.2	1.36E-09	1.00E-10	7.35E-02	5.00E+00	1.22E+00	8.97E-02	0.05
Sulphur											
OF	180	60	4.00E-10	35.3	6.80E-10	2.00E-10	2.94E-01	5.00E+00	1.00E+00	2.94E-01	
11 ppm	180	80	1.20E-09	47.1	2.04E-09	1.00E-09	4.90E-01	5.00E+00	1.00E+00	4.90E-01	
Sulphur	180	100	4.50E-09	58.8	7.65E-09	2.00E-09	2.61E-01	5.00E+00	1.00E+00	2.61E-01	0.4
OF	215	80	5.00E-09	47.1	8.50E-09	1.00E-08	1.18E+00	5.00E+00	1.00E+00	1.18E+00	
11 ppm	215	60	7.50E-10	35.3	1.28E-09	1.00E-09	7.84E-01	5.00E+00	1.00E+00	7.84E-01	
Sulphur	215	40	1.00E-10	23.5	1.70E-10	1.00E-10	5.88E-01	5.00E+00	1.00E+00	5.88E-01	0.85
OF	215	80	7.00E-09	47.1	1.19E-08	1.00E-08	8.40E-01	5.00E+00	1.00E+00	8.40E-01	
11 ppm	215	70	5.00E-09	41.2	8.50E-09	8.00E-09	9.41E-01	5.00E+00	1.00E+00	9.41E-01	
Sulphur	215	45	5.00E-10	26.5	8.50E-10	1.00E-10	1.18E-01	5.00E+00	1.00E+00	1.18E-01	0.63
OF	215	100	5.00E-08	58.8	8.50E-08	6.00E-08	7.06E-01	5.00E+00	1.00E+00	7.06E-01	
6 ppm	215	80	2.00E-08	47.1	3.40E-08	1.00E-08	2.94E-01	5.00E+00	1.00E+00	2.94E-01	
Sulphur	215	55	2.00E-09	32.4	3.40E-09	4.00E-10	1.18E-01	5.00E+00	1.00E+00	1.18E-01	
	215	40	5.00E-10	23.5	8.50E-10	1.00E-10	1.18E-01	5.00E+00	1.00E+00	1.18E-01	
	215	70	4.00E-09	41.2	6.80E-09	7.00E-09	1.03E+00	5.00E+00	1.00E+00	1.03E+00	0.45
OF	250	20	9.70E-11	11.8	1.65E-10	5.00E-12	3.03E-02	5.00E+00	1.00E+00	3.03E-02	
11 ppm	250	40	5.70E-10	23.5	9.69E-10	7.00E-10	7.22E-01	5.00E+00	1.00E+00	7.22E-01	
Sulphur	250	60	3.00E-09	35.3	5.10E-09	1.00E-08	1.96E+00	5.00E+00	1.00E+00	1.96E+00	0.91

3.4 Life prediction

Forsberg refers to the deformation map of Frost and Ashby (figure 1 of this report) and quotes a predicted a life of 84,000 years for OF material tested at 100 ºC and 40 MPa. which was taken from unpublished work by Pettersson. On the assumption that the strain rate in OFP is 100 times lower and fracture strains are equal he claims that OFP will have an almost infinite life. Details of the calculation are not given and as the Frost and Ashby map predicts strain rates, it is necessary to make an assumption about failure strain in order to predict a life. The comparison of predicted strain rate for OF material with observed strain rate referred to in 3.3 above adds some confidence to the prediction of life for OF material under service conditions.

It is unsafe to assume however that the 100 times lower strain rates which have been observed between OF and OFP materials under specific test conditions will also occur under the canister service conditions. It is also unsafe to assume that the fracture strain measured on OFP in one test condition will also apply in the canister service condition. The longer life suggested for OFP cannot be justified on the arguments provided.

The information which is needed in order to make a realistic life estimate includes the strain rates and fracture strains which would be achieved with OFP at 100 ºC in the power law regime.

4. Conclusions

1. Storage conditions for the copper-iron canister are likely to include stresses up to 50 MPa and the possibilities of creep failure of the copper shell cannot be discounted.
2. Creep failure strains for OF and OFP copper decrease with decreasing stress. In the power law breakdown regime (that is roughly for stresses exceeding 100 MPa) the range is from 50 % to 10 %. OF copper exhibits brittle behaviour in the power law regime (that is roughly for stresses less than 100 MPa) with failure strains falling to less than 5 %. This behaviour renders it unsuitable for use in the copper–iron canister.
3. No satisfactory tests have been conducted on OFP material in the power law regime. There is no evidence that fracture strains for this material will or will not continue to decrease with decreasing stress in this range.
4. Attempts to measure fracture strains and secondary creep rates for OFP material in the power law regime have been frustrated by the very long test times which are required at representative temperatures.
5. When test temperatures for OFP are increased to 300 ºC or more in the power law regime, there is evidence of grain boundary cavitation, which at lower temperatures would be accompanied by low strain to fracture failures. In these cases however fractures are mainly ductile. This ductility is unlikely to be reproduced at lower test temperatures.
6. Raising the sulphur content of OF copper from 6 ppm to 10 ppm causes further reductions in failure strain in tests carried out under power law conditions but not under power law breakdown conditions. There is no reason to suppose that OFP material will not behave in the same way.
7. The cause of the further reduction in ductility referred to in 6 above is segregation of sulphur to crack nuclei in grain boundaries and this is why it does not occur under power law breakdown conditions where failure is transgranular. It does not occur in the timescales so far considered when sulphur content is 6 ppm.
8. For OFP material the stress level required for a given creep rate in the power law breakdown regime at 215 ºC is much higher than that required for pure material according to figure 1. Predicted strain rates for OF material are in good agreement with the observed values for a wide range of test conditions in the power law and power law breakdown regimes.
9. Predictions of satisfactory creep lives for OFP material in service are only reasonable providing that the OFP material does exhibit the same increased resistance to deformation in the power law regime as has been observed in the power law breakdown regime and does not exhibit the same changes in fracture strain observed in OF material on changing from power law breakdown to power law behaviour.

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7. Appendices

7.1 Appendix A. Stresses on the canister

7.1.1 Residual stresses from manufacturing

Josefson et al (1993) and co-workers have used finite element methods to calculate the internal strains that might arise in the canister during manufacture and these have also been reported by Nilsson (1992). Two main strain concentrations are referred to and both are related to electron beam welding. The first is in the vicinity of the weld itself and the strain predicted corresponds to a peak stress of 60 MPa. The second, which is close to the backing ring, involves an accumulated local plastic strain of 5 % in the vicinity of the weld which corresponds to stress of 140 MPa. (Lindblom et al., 1992). Nilsson (1992) indicated that the peak stress of 140 MPa may be reduced considerably by attention to design. It should also be suggested that a change from electron beam welding to Friction stir welding could lead to a considerable reduction in internal stress.

Following the work of Lindblom et al (1992), Nilsson (1992) goes on to say that an initial rapid reduction in internal stress occurs during the first 100 hours after manufacture when the external temperature of the canister is likely to be 150 ºC. Stress relaxation experiments carried out by Lindblom (1992) and co-workers indicate that at 150 ºC tensile stresses as high as 250 MPa are relaxed almost instantaneously to less than 50 MPa. Such stresses are further reduced to less than 40 MPa in 100 hours. Similar tests at 150 MPa and 75 ºC indicate that the instantaneous stress relief is to 75 MPa with a further fall of approximately 30 % over 500 hours.

These stress relaxation observations are not predicted accurately by figure 1. The reason for this is, partly, that in this range of temperature and stress, strain rate shows an extreme sensitivity to stress. Figure 1 predicts that at a tensile stress of 140 MPa and a temperature of 150 ºC the strain rate is of order 10^{-8} per second which requires 70 days for a 1 % strain relaxation. At a stress of 180 MPa and 150 ºC the predicted strain rate is 1 per second whilst at 75 MPa it is 10^{-9}per second. This sensitivity, indicates the need to use results from experiments on the practical materials if relaxation time predictions in these high stress ranges are to be credible.

The Lindblom et al (1992) work included elevated temperature tensile tests. The results of tests at 150 ºC indicate that the instantaneous stress relaxation from 250 MPa to less than 50 MPa corresponds to relaxation by plastic flow to a residual elastic strain of order 0.1 %. Youngs modulus for the material appears to have been insensitive to temperature over the temperature range 26 ºC to 250 ºC. At 26 ºC and 100 ºC the stress for 0.1 % strain was close to 75 MPa. We may therefore assume that it would be almost the same at 75 ºC. On that basis it is concluded that the instantaneous stress relaxation at 75 ºC and 75 MPa also corresponds to a residual elastic strain of 0.1 % and that the stress relaxation behaviours at 100 ºC and 75 ºC are similar.

All the above work was carried out on Cu-OFP material with a grain size of 45 µm. There was no evidence in the tensile tests for a low strain to fracture failure mechanism.

It is assumed that the high initial stresses used in stress relaxation tests were achieved by instantaneous loading and relieved by a process of dynamic recovery. The same dynamic recovery process will prevent the high residual stresses calculated for the post welding state to be realised but the predicted strain will be realised and its effects must be considered. There is every reason to believe that the effects of the recovery mechanism occurring in the tensile tests is similar to that occurring to relax the welding stresses and there is no reason to suspect that mechanisms leading to low strain to fracture failure will operate in the CuOFP material under these conditions. That is not to say that a coarse grained sulphur bearing copper would not exhibit low strain to fracture effects or that CuOFP would not exhibit low strain to fracture effects under different conditions of load, time and temperature.

In a later work Josefson (1992) used a finite element approach to consideration of stress relaxation after welding but before deposition, i.e. over the first 100 hours. His predictions for stress relaxation before deposition were roughly in line with those given above. He used representative stress relaxation creep results to calculate values for the B and n parameters in the Norton-Bailey equation during the waiting period, the values were of 3.5×10^{-41} and 20 respectively. These are not typical of power law creep but they did provide good agreement with experimental observation in stress relaxation tests at temperatures and stresses which were selected to represent the waiting period.

An important observation from the Josefson (1992) work is that the peak combined plastic and creep strain close to the corner near the weld is predicted to be 14 %, 100 hours after welding is completed.

From these observations it is reasonable to conclude as follows.

1. Welding and stress redistributions which occur in the holding period will cause local strains, which could in the worst case be as high as 14 %.
2. Owing to dynamic recovery during and immediately after welding and the high temperature in the immediate post welding period, stresses arising from the welding strains will be relaxed rapidly to levels which correspond to 0.1 % strain at the ruling temperature (this is approximately 75 MPa at 100 ºC or 50 MPa at 150 ºC). A further 30 % stress and strain relaxation will occur during the first 20 days after welding the lid and the relaxation after this time will continue at a reducing rate with time. It is to be expected therefore that the peak internal stress at the time of placing in the repository will be close to 50 MPa.
3. A further 30 % stress and strain relaxation will occur during the first 20 days after welding the lid and the relaxation after this time will continue at a reducing rate with time.
4. The location of the peak strains will be close to the lid corner on the inside of the copper shell.

7.1.2 After deposition

The loads which might arise in the repository environment have been considered by Werme (1998).

The normal load case given is 14 MPa pressure (including “customary” safety margins). This is made up of 7 MPa hydrostatic pressure and 7 MPa swelling pressure of the bentonite.

The hydrostatic pressure from a 500 m head is close to 5 MPa and from this we calculate that the safety factor used in this case is plus 40 %.

An accurate determination of the maximum combined stress arising from residual welding stresses, hydrostatic pressure and bentonite swelling and relaxation processes is beyond the scope of this work. It is clear however that the hydrostatic and swelling pressure components build up over a long time period estimated to be no less than ten years. Bearing in mind the rapid rate of reduction of residual stresses to the 0.1 % proof stress observed for the holding period, it is reasonable to assume that for the base case the build up of localised stresses arising from swelling and hydrostatic components will be less than the rate of relaxation. Thus the peak localised stresses should never exceed the level present at deposition. This general view is supported by the early work of Josefson et al, 1993 who used finite element methods to calculate the combined effects of stress relaxation and repository pressure build up. Over time the overpack will collapse completely onto the liner and the whole system will be subject to the uniform swelling pressure, the peak strains involved in this process have not been calculated.

Residual stresses close to the bottom weld will be lower than residual stresses near the lid weld owing to the longer relaxation time before deposition. Thus although stress concentrations will develop at the bottom corners of the canister they will not exceed the residual stresses present close to the lid weld.   It is safe therefore to assume that the residual stresses present at deposition will not be exceeded during the period of pressure build up to the normal load case.

The allowance for bentonite swelling pressure is uncertain however. As it is very important to consideration of the type of creep deformation which will occur it has been considered in more detail in Appendix B.

The conclusion in appendix B is that hydrostatic plus swelling pressure can not be allowed to exceed 40 MPa in the interest of preventing plastic collapse of the liner. Such a pressure if it could occur would also build up over at least ten years. Collapse of the overpack onto the liner will lead to stress concentrations but such stress concentrations would be subject to being relieved by flow just as the welding stress concentrations are during the holding period. When flow has occurred sufficiently for contact between the overpack and the liner to be complete then, for the uniform swelling case the whole of the overpack will adjust to a uniform compressive stress equal to the external pressure and no further deformation will occur. It is safe therefore to assume that even if the bentonite swelling pressure reaches the maximum value of

40 MPa the peak stresses in the overpack during storage will not exceed the stresses present at deposition.

The base case discussed above may be regarded as pseudo-steady state after saturation of the bentonite but account has to be taken of uneven pressure build up in the water saturation phase which may lead to tensile or compressive stresses in the canister. These forces do not contribute to the collapse mechanism for the liner which was discussed in the previous paragraph. Three bounding cases are discussed by Werme. Simple calculations in which the bentonite is assumed to resist deformation, yield very high bending stresses on the canister which could lead to failure. However when the calculations are refined in a finite element scheme, which takes account of the properties of the bentonite, the peak tensile force in the canister insert is limited to 55 MPa. This indicates that under conditions where supply of water to the bentonite is non-uniform, non-uniform swelling will lead to flow in the bentonite to relieve swelling pressure. Peak swelling pressure will not be achieved until the bentonite is fully saturated but the bending moments on the canister which arise from swelling will peak at some time before complete saturation is reached, that is to say sometime in the first 10 to 100 years. Whilst the 55 MPa tensile force should be safe on the insert, the effect of the unbalanced force on the copper will be to make it flow in the same way as the bentonite. The magnitude of the tensile stresses which would develop in the copper is not given by Werme and it is beyond the scope of this work to calculate it. However it seems unlikely that it would exceed the peak stress of 55 MPa which is calculated for the liner.

An alternative scenario where saturation proceeds from the bottom of the emplacement hole to the top, imposes shear forces on the copper, these forces will depend on the swelling pressures and are subject to the same uncertainty. The maximum axial stresses induced in the copper for the conditions studied (which included a peak swelling pressure of 8 MPa) was 19.3 MPa. The shear stresses arising from this axial stress were not calculated but bearing in mind the high surface area of the canister compared to the cross sectional area of the overpack it is clear that they will be low. Even if the swelling pressure is increased by a factor of five (to the maximum permissible by the collapse pressure for the liner) the shear stresses will still be low.

Finally the effect of ice loading which arises in a future ice age has to be considered. The ice load, when it occurs, will be additive to the swelling pressure at that time.

The extreme case corresponding to an ice-cap 3 km thick adds 30 MPa hydrostatic pressure to the base case. As it is a hydrostatic pressure and it is not likely to occur until after the effects of residual stresses have disappeared it may be considered as additive to the swelling pressure but of no consequence as far as creep of the copper overpack is concerned.

Considering all these points it is concluded;

5. That the uniform pressures which might arise from ideal bentonite swelling, hydrostatic pressure and the ice load should not cause a creep problem by virtue of the fact that they are hydrostatic.

6. Collapse of the overpack onto the liner will lead to localised stress concentrations but their rate of development will be such that the localised stresses present at deposition will not be exceeded.
7. Non uniform swelling of bentonite can lead to localised stress concentrations but their levels will not exceed the stress concentrations present at the time of deposition. Peak localised stresses should not therefore exceed 50 MPa.

In his discussion of localised stresses Josefson (1992) argues that the Norton-Bailey parameters given for the holding period would not be appropriate for consideration of long term creep in the repository and that the governing process in this stage would be volume diffusion. Values of B and n suggested are 2.7×10^{-20} and 5 respectively. These are calculated from creep tests at temperatures around 100 ºC and 100 MPa. They would be typical of power law creep. At later stages when temperature in the repository declines and residual stress has further declined, it is suggested that the dominant mechanism may be surface diffusion. No B or n value is suggested for this stage.

The Josefson view (above) is supported by the results of Lindblom et al. (1992) which indicate an activation energy for stage two creep under these conditions of 197 kJ/mol. which corresponds to self diffusion and is consistent with a mechanism involving dislocation glide but with vacancy assisted climb as the rate controlling step. A single result on a test carried out at 100 ºC does not fit with the higher temperature results and this is attributed to the extremely low creep rates at that temperature (it is suggested that second stage creep had not begun).

Nilsson (1992) agrees that creep deformation after deposition will occur due to external pressure and suggests that this creep should *involve* diffusional flow.

Further conclusions are therefore as follows.

8. During long-term creep in the repository the dominant creep mechanism power law creep with activation energy of 197 kJ/mol. In this stage the creep mechanism is dislocation glide with vacancy assisted climb as the rate controlling step.
9. In the very long term when stresses and temperatures both decline the creep mechanism is likely *to involve* diffusional flow.

7.2 Appendix B. Bentonite swelling pressure

Werme (1998) quotes and reproduces the work of Pusch and Börgesson in his design premises paper. These workers indicate that swelling pressure of the bentonite is a function of porosity, initial water content, available expansion space and degree of saturation achieved. This is because the swelling pressure will depend on, the volume of free space available between the bentonite blocks or pellets and the cavity into which they are emplaced, the water contents and porosities of the blocks and pellets as manufactured, and the amount of water taken up. On this basis it may be predicted that if the free space for expansion of the bentonite is high, saturation will occur with no increase in pressure. If it is too low a maximum pressure will be developed at which no further uptake of water will be possible. This will be the equilibrium pressure for a system of partially saturated bentonite and free water under the prevailing temperature conditions.

In the repository it is planned that a gap of 10 mm will be left between the walls of the canister and the bentonite blocks and a further gap of 50 mm will be left between the blocks and the rock. This latter space will be filled with bentonite pellets. The free space for expansion is thus made up of the porosity in the bentonite blocks and pellets, the packing density of the pellets and the gap between the blocks and the canister.

It appears that the range of initial water contents and densities of the bentonite blocks as well as the spaces between the blocks and the canister and the blocks and the rock are limited by practical considerations. These include the handling characteristics of the blocks and pellets as manufactured, and their mechanical properties. They must resist serious damage due to handling and they are required to have adequate resistance to deformation under their own weight (in the cavity) or the weight of the filled canister. This is to ensure the stability of the canister position in the rock cavity and to preserve the expansion space.

In order to achieve maximum resistance to deformation and good handling characteristics it is desirable to use low initial water content and a high compaction pressure. These manufacturing conditions will result in the highest swelling pressures in the bentonite during saturation.

Pusch and Börgesson have calculated swelling pressures and final density at saturation under the packing conditions which are planned for the repository. They examined three cases where initial density (dry density), initial water content and compaction pressure were varied. They calculated that for the highest practical compaction pressures (500 MPa) and lowest initial water contents (10 %), swelling pressures of 100 MPa should be expected. Increasing the initial water content to 17 % produced a reduction in the swelling pressure to 30 MPa. A reduction in compaction pressure at 17 % initial water content led to a further reduction in swelling pressure to 13 MPa. Pusch and Börgesson state that if a design swelling pressure of 7 MPa is to be achieved then either smaller blocks (presumably with spaces between them) or blocks made with lower compaction pressures would be required. No comment is made on the likely mechanical properties of such blocks or of their stability in the repository.

It is clear that there is considerable doubt that the maximum swelling pressure can be limited to 7 MPa and that swelling pressures of up to 100 MPa are possible. At this point therefore we are only able to conclude that the force driving creep of the copper overpack onto the canister for the normal load case is between 12 and 112 MPa with no allowance for safety factors.

However Werme also refers to work by Ekberg which is published in the Swedish language. This work calculates the critical pressures for canister collapse to be 81 MPa for the BWR version and 114 for the PWR version (the difference arises from the configuration of the internal supports). From this observation we conclude that if the peak pressures including safety factors cannot be maintained below 81 MPa then a major redesign of the canister is required.

For the purpose of this study and in order to leave a 50 % safety margin against canister collapse through material defect, we must assume that the peak pressures (arising from hydrostatic and bentonite swelling components) will not exceed 40 MPa and that the design of the bentonite filling system will meet that constraint. The bentonite swelling pressure must therefore be limited to less than 35 MPa.