SKI Report 98:29

Design Basis For The Copper/Steel Canister

Stage Four

Final Report

W H Bowyer

Meadow End Farm, Tilford, Farnham, Surrey. GU10 2DB. England

June 1998

SUMMARY

The development of the copper/iron canister which has been proposed by SKB for the containment of high level nuclear waste in the Swedish Nuclear Waste Disposal Programme has been studied by the present author from the points of view of choice of materials, manufacturing technology and quality assurance. Earlier reports[1, 2,3] describe observations made in the period to April 1997.

This report describes the observations on progress that has been made between May-1-1997 and April-30-1998 and the result of further literature studies. SKB have allowed the author access to certain of their subcontractors for discussions and observations of progress and have provided certain contractor reports for review. This has been supplemented by a literature study and discussions with other consultants.

Cast steel has been rejected in favour of cast iron as a candidate material for the load bearing liner. Nodular (or ductile) iron is selected and this is capable of providing mechanical properties which are equally suitable as those of the originally selected high strength low alloy steel. Developing the suitable properties in the cast iron component depends on the design of the casting, the precise composition of the material and the casting conditions. The optimum combination of these parameters is usually determined experimentally in the development programme.

The material specified for the overpack is OF (Oxygen Free) copper with 50 ppm of phosphorus added. It is recognised that the processing of the OF copper to a satisfactory final component may require that the levels of residual elements in the material may have to be specified much lower than the OF specification permits. SKB have decided that the specification can not be finalised until the manufacturing procedures are defined.

Some basic work, on creep characteristics of coarse grained material, on recrystallisation characteristics and segregation of impurities to grain boundaries is in progress and the results of this work will impact on the final choice of material and on the manufacturing route.

Corrosion studies supported by SKB indicate that in the absence of mechanical failure or accelerated localised corrosion the overpack should provide corrosion shielding of the canister for its full design life. An inner vessel made of carbon steel would develop a magnetite coating which would act as a protective layer against further corrosion if the copper overpack is breached during the anaerobic period of the repository life. Such a layer would be self healing if it were damaged superficially. Unfortunately the liner will not be made of carbon steel. Published work claiming that the nodular iron liner would have corrosion characteristics similar to the carbon steel which had been examined in depth is flawed since the microstructures of the iron and carbon steel specimens used were not investigated. It is highly unlikely that nodular irons in the form used for the experiments would have similar structures to nodular iron in the canisters by chance.

If the overpack were breached during the aerobic period of the repository life then very rapid penetration of the inner liner could occur. The duration of the initial aerobic period of the repository life is not defined and early assertions that it would be very short owing to the need for mass transport of oxygen by diffusion in bentonite are described as unrealistic in the later work.

Factors which might cause breach of the overpack include, accidental damage during emplacement, creep during collapse of the outer vessel onto the inner or due to unbalanced

swelling of the bentonite, or localised corrosion arising from defects in the overpack such as segregation of impurities, crevices, cracks or cavities in the vicinity of welds.

Several full size castings of the inner vessel have been made and they are dimensionally satisfactory. One is being subjected to metallurgical examination and the remainders are being allocated to experiments at the Äspö laboratory and public relations activities. The development of the castings will continue when these activities are complete. Similarly a number of overpacks have been made by the fabrication method for use in experiments. These are not being subject to detailed metallurgical examination. It has been recognised that the roll forming method is not suitable for serial production and alternatives are being sought. Two candidates which are under investigation are extrusion and a pierce and draw process which is similar to backward extrusion. Both these methods are more suitable for serial production and there is a reasonable prospect that either may be developed to provide a satisfactory metallurgical structure. A further option under investigation is reduction of the thickness of the overpack from 50 mm to 30mm.

The electron beam welding process has been explored with tenacity but has so far failed to produce a satisfactory lid weld. It is probable that a prime reason for the difficulty arises from the zone refining action of the process. A new welder is being developed for supply to the SKB pilot plant where development will be continued. An alternative welding process, friction stir welding, is being examined as a candidate for attaching lids. This is potentially a more favourable process than electron beam welding but it is in an early stage of development.

Surface breaking defects may be detected using eddy current methods but there is currently no reliable way of detecting small sub surface defects in the overpack. The performance of ultrasonic systems has been examined and understood. Improved methods are under development but the timescale for completion is indefinite.

There is no readily available literature relating to manufacturing defects in copper, which is relevant to the canister production. It is appropriate to document experience gained in the development programme and in production for quality control purposes.

CONTENTS

DESIGN BASIS FOR THE COPPER CANISTER STAGE FOUR

1 INTRODUCTION

This is the final report on stage four of a consulting assignment aimed to assist SKI in understanding and reviewing the work of SKB on the development of the composite canister for long term storage of high level nuclear waste.

The intended activities in the 1997/98 assignment were;

1. Continuing liaison with, SKI contractors including Wyman-Gordon, VSEL and TWI. This includes discussion of and where it can be arranged observation of technology trials. The purpose of these liaisons were, to understand and report on the technology developments, to observe the quality of the starting materials and the non destructive testing procedures and to report on the effects of processing on the microstructures and the properties of the materials used.

2. Reading and commenting on reports supplied by SKI, mainly from SKB and their contractors.

3. Monitoring the production of cast liners, commenting on casting technology, quality and quality assurance procedures. This included meetings at the selected foundries.

4. Carrying out a study on the defects which occur in OF and OFE coppers through consultation with Industry.

5. Attending and reporting on the MRS meeting in Davos, Switzerland, in September/October 1997.

6. Commenting on SKI commissioned studies on annealing of OF copper at the University of Linköping.

7. Attending four discussion meeting in Sweden to report on progress and to support SKI in interpretation of further work on galvanic attack, creep, Stress corrosion and annealing in coarse grained material of the selected composition which was to be carried out on behalf of SKB or SKI.

In the event it has not been possible to monitor progress in UK based organisations as detailed in item 1 but, SKB have hosted a number of alternative information transfer meetings at their premises in Stockholm and at the works of Swedish contractors. All these activities and the observations arising from them are reported in the following sections.

2 PROGRESS ON CANISTER DEVELOPMENT

2.1 Materials Selection

2.1.1 The Load Bearing Liner

An earlier report[3], discussed the reasons for changing from a fabricated steel liner to a cast liner and a first experiment on the production of a half height cast liner in steel, at the Kolswa foundry in February 1997. It was reported that whilst there were some obvious problems with this first attempt SKB were encouraged and intended to proceed to the production of a full size component.

SKB recognised that it would be necessary to section the casting on several longitudinal and transverse axes to examine the soundness of the casting with reference to cavities caused by inadequate feeding and to examine the residual stresses which could lead to extension of cracks which were clearly visible on the machined surfaces.

SKB agreed to share information derived from sectioning and metallurgical investigation of the first casting when it becomes available. This has not been done on a formal or complete basis but,
in a private conversation Lars Verme of SKB revealed that the cast inner liner had serious shrinkage defects which were discovered when it was examined in more detail.

The shrinkage defects are assumed to be cracks and cavities in the casting referred to earlier. Their severity was expected by the present writer[3], " since solidification of the casting from the outside in, leads to the development of tensile stresses on the inside and compressive stresses on the outside of the casting. The magnitude of these stresses may be visualised by recognising that the foundryman makes an allowance of up to 4% for shrinkage during cooling of steel castings". The cavities in steel castings arise mainly from inadequate feeding of liquid metal to offset solidification shrinkage and they are expected mainly in heavy sections remote from the feeders and possibly all the way into the feeders.

The alternatives to steel castings considered by SKB were nodular cast iron or bronze and the experience with steel clearly persuaded SKB to examine these. There are few foundries in the world with capacity or experience of making castings of the required size in bronze. The writer located several who were prepared to try and SKB were advised, however they decided, rightly in the view of the writer, that cast iron would be a better choice and a foundry experienced in production of rolls for the paper industry was engaged to carry out trials. The results of these trials will be discussed in section 2.3.2.

The reason for choosing cast iron over steel is mainly on its more favourable shrinkage characteristics and this has been discussed in an earlier report[2]. Cast iron is a class of materials and the particular member of the class selected is ductile or nodular iron. This is distinguished by an as cast microstructure in which graphite is present as nodules rather than the flakes which are characteristic of grey iron. The flake form of graphite is largely responsible for the serious lack of ductility (1 – 6%) exhibited by most cast irons. The nodular form of graphite is achieved by the use of purer starting materials (principally a lower sulphur content), by the adddition of specific amounts of magnesium and or cerium to the melt and by control of cooling rate. Good nodular irons with a ferrite matrix would have a ductility of 18% minimum coupled with a tensile strength of 415 MPa. A grey iron of this strength would have a ductility of 0.6 %. Through controled cooling or heat treatment of ductle iron, the strength may be icreased up to 100 MPa with a consequent reduction in ductility to around 1%. In heavy castings control of cooling rate may be very difficult after casting or after heat treatment and for this reason such castings are used in the as cast condition. A material similar to that specified by SKB which is also specified for paper making drier rolls would be used in the as cast condition and would have a strength of 550 MPa coupled with a ductility of 3 % when cast in a 50mm section in a sand mould. The analyses of the canister material (SS 07-17 iron) specified by SKB and the material referred to above (ASTM A476-70(d); SAE AMS5316) are given below.

	C%	Si%	Mn%	P% (max)	S% (max)	Ni%	Mg%
Canister material	3.2	1.5-2.8	0.06-1.0	0.08	0.02	0-2.0	0.02-0.08
Paper roll material	3.0 min	3.0 max	-	0.08	0.05	-	-

The cast steel specified by SKB for trials and rejected would be expected to have a tensile strength of 450 –500 MPa with a ductility of 25-30 % and the high strength low alloy steel specified for the fabricated liner would be expected to have similar properties.

There is therefore a penalty in mechanical property terms in changing from fabricated steel to a cast iron canister. This penalty is in ductility rather than in strength and, in the opinion of the writer, providing that the casting is of good quality this should not represent a problem. Opinion is not a satisfactory basis on which to accept or reject a design however and at some stage it will be necessary to provide a mechanical property specification for the cast iron and the composition range to achieve it. Since the acceptable composition range is dependent on the shape and size of casting it is usually determined by the production and testing of trial castings. The testing includes determination of mechanical properties and structure of specimens taken from representative areas of real castings as well as determination of the effects of casting variables on the degree and location of shrinkage effects (cracking and porosity).

It will also be necessary to define the required level of integrity of the outer shell and the required level of support from the internal structure. It may be that no support is required from the internal structure providing that the total porosity distributed in the outer shell does not exceed a given value, that there are no clusters of porosity exceeding a given volume and that no individual pores exceed a certain size. This will be referred to in section 2.2.1 on technology development.

2.1.2 The Copper Overpack

2.1.2.1 Specification

The specification for the copper of the overpack has been referred to in earlier reports[1,2,3]. The most recent of these[3] reported that SKB had adopted the OF(E) grade with a 50-ppm phosphorus addition. A clarification from SKB at a meeting in the offices of SKI (April 1997) indicates that this is not so. The specification is OF plus 50-ppm phosphorus. Supplies of OF plus 50-ppm phosphorus from Outokompu Pori however have composition conforming to OF(E) with 50-ppm phosphorus added. Supplies from other companies would not necessarily conform to the OF(E) specification and thus, unless Outikompu-Pori is specified as the sole supplier, at this stage it should be assumed that the OF(E) specification will not be met. For completeness a table showing the compositions of relevant grades and specifications which has been reported previously[3] is given in Table 1(page 12). Early tests indicated that material to the OF specification could exhibit unacceptably low creep strain to failure which was related to sulphur seggregation. Consequently the specification was changed by SKB to OF copper with 50 ppm of Phosphorus added and 7ppm max sulphur content. This was on the basis that the phosphorus addition would increase creep resistance and the 7ppm sulphur would be too low to cause the low creep strain to fracture mechanism. In a very limited number of tests, SKB demonstrated that for fine grained copper with 7 ppm sulphur, adding 50 ppm phosphorus led to a clear improvement in the creep-strength and creep strain to fracture. It is understood that further work has been put in hand by SKB to determine whether or not the improvement in creep strain to fracture can be reproduced by the same means on coarse grained material similar to that which is expected in the overpack. No results have so far been reported. This remains a matter of concern since it is argued[2] that grain boundary area is in inverse proportion to grain size, thus the concentration of sulphur in grain boundaries for any total sulphur content will be in direct proportion to grain size. The critical level of sulphur for initiation of the low creep strain to fracture mechanism is therefore expected to be grain size dependent. The critical level of sulphur for material of grain size up to 100 microns is 7 ppm. The grain size in the overpack material is currently expected to be up to 500 microns.

Recent work funded by Posiva at VTT[4] has considered creep properties of OF copper containing electron beam welds. It concluded that the cross weld fracture strain under repository conditions would probably exceed 5 percent whilst the expected maximum strain in service is expected to be 2 percent. A detailed review of this work is given in section 8.9. It is unacceptable to extrapolate this conclusion to the case of the SKB canister, even though the material tested was coarse grained. The reasons for this are;

1. that the work was based on too few specimens and involved extrapolations which were too extreme for the conclusions to be accepted.
2. The electron beam welds were high vacuum electron beam welds, which are not similar to the welds proposed by SKB.
3. Only the weld material was tested,(because failure always occurred in the welds) and
4. The electron beam welding process would zone refine the weld metal to remove sulphur which is the element responsible for the low creep strain to fracture problem.

The effects of impurities and coarse grain sizes in OF copper have been summarised in earlier work[3]. In view of the coarse grain sizes which arise as a result of processing and the fact that the corrosion properties (including crevice corrosion and galvanic attack) and the tendency towards hot shortness and cold shortness are influenced by segregation of impurities to grain boundaries, it has been suggested[2,3] that it may be necessary to specify lower levels of impurities in the canister material. Hot and cold shortness which is directly attributable to seggregation of impurities to grain boundaries has been observed in the manufacturing trials[3] , unfortunately the detailed composition of the specimens exhibiting these effects is not available but it was claimed to conform to the OF specification with 50 ppm phosphorus added.

Table 1 (overleaf) and the following notes are reproduced with minor modifications from the earlier report[3].

The first section compares the specifications for grade one cathode in the British and US standards with the standards achieved in production by a British company (IMI) and a Finnish company Outokumpu.

In the centre of the table the ASTM standard for Oxygen Free Electronic (OFE) grade is compared with the proposed new European standard for Oxygen Free Electronic made from

Table 1 Comparing ASTM and BS specifications on impurity levels with current industrial production

	ELEMENT ppm																				
ALLOY	P	Se	Te	Bi	Sb	As	Sn	Pb	S	Ag	O	Fe	Cd	Mn	Cr	Si	Zn	Co	Hg	Ni	Total impurity ppm
Cathode BS 6017	-	2	2	2	4	5	-	5	15	25	-	10	-	-	-	-	-	-	-	-	65
Cathode ASTM B115-83a	-	4	2	2	5	5	10	8	25	25	200	-	-	-	-	-	-	-	-	-	90 exc. O
Cathode 1 (IMI Walsall)[5]	-	<0.3	<0.1	<0.8	<1.0	0.6	<0.3	<2.0	5	13	-	4	0.1	0.2	<0.5	0.5	<1.5	<0.5	-	1	31.4
Cathode 2 Outokumpu[6]	-	<0.2	<0.1	0.5	1.4	1.2	-	<1	5	12	-	<1	-	-	-	-	-	-	-	-	
OFE-ASTM	3	3	2	1	4	5	2	5	15	25	5	10	1	0.5	-	-	1v	-	1	10	100
OF Ec (Draft EU Standard)[7]	3	2	2	2	4	5	2	5	15	25	a	10	1	5	-	-	1	-	-	10	100
PHCEc (Draft EU Standard)	60	2	2	2	4	5	2	5	15	25	-	10	1	5	-	-	1	-	-	10	100
Outokumpu OFE-OK	1	1	1	0.5	-	-	0.5	1	0.6	-	1.5	-	0.5	-	-	-	0.5	-	-	-	30
Outokumpu OF-OK	10	2	2	2	4	5		5	15	25	3	5	1						1		100
OF (Draft EU Standard)	-	-	-	5	-	-	-	50	-	-	a	-	-	-	-	-	-	-	-	-	500
PHC (Draft EU Standard)	60			5				50											-		500
HCP (draft EU Standard)	70			5				50											-		500
PDO (IMI Walsall)	213	<1	<1	<1	1	2	2	2	6	11		19	<1	<1	<1	1	<2	<1	-	4	270

Cathode (OFEC) and the proposed new European standard for PHEc (Phosphorus bearing High Conductivity made from cathode). All these have a maximum total impurity level of 100 ppm. The final member of this group is the current Outokompu OFE grade. This grade is made from pure cathode and has virtually the same composition which, at 30-ppm total impurity, is well inside the standard.

The final group in table 1 includes the proposed new European standard for OF (Oxygen Free), PHC (Phosphorus bearing High Conductivity) and HCP (High Conductivity with Phosphorus), they are compared with the current production values for PDO (Phosphorus DeOxidised) from IMI and OF from Outokumpu. This is the standard that the test materials used by SKB and their contractors to date ordered to[2], it allows a high degree of flexibility (in order to cope with variations from different ore bodies) within the overall total impurity limit of 500 ppm. It is clear that there is very little difficulty for the copper producers in supplying to impurity levels well inside the standards for all the grades considered.

In view of the changes in quality specification which SKB have made during the development programme and the wide scope for variation of impurity levels which may be supplied within the specifications, it will be necessary for SKB to be more precise about their specification. They have already acknowledged this by specifying 7 ppm max sulphur (Outokompu OF-OK specifies 15ppm max). It may also be necessary to place tighter limits on the levels of elements such as lead and bismuth.

2.1.2.2 The Effects Annealing on Grain Size and Seggregation of Impurities

The effects of impurities in OF copper have been dealt with in detail in an earlier report[3] and will not be repeated here.

In view of concerns related to, hot shortness, cold shortness, creep effects, possible galvanic attack, crevice corrosion, stress corrosion and critical strain grain growth, all of which are influenced by impurity seggregation, a short research exercise to determine the effects of cold working and annealing on final grain size and the effects of grain size on impurity seggregation has been initiated at the University of Linköping under the guidance of Professor Torsten Ericsson.
Three meetings have been held with Proffessor Ericsson in the current reporting period to review progress and plan future work.

In the first meeting a preliminary exercise was discussed. This work demonstrated the effectiveness of the strain-anneal technique in producing a range of grain sizes and that a range of strain levels may be achieved in a single tapered specimen by loading to a selected level in tension. Material from the SKB programme was used in order that the results would refer to the practical case. Unfortunately failure to bring the material to a standard fine-grained condition before starting the work, prevented any meaningfull quantitative observations from being made. It was agreed that the results from this work would be used to help plan a second exercise, which would be the subject of a further research proposal.

A further proposal was prepared by Professor Ericcson, this led to a second meeting in which the detailed procedures required to achieve the required results were discussed and agreed. It was agreed that a further supply of material would be obtained and that this would be cold reduced in three stages from a starting plate thickness of 60 mm to a sheet thickness of 6 mm. The intermediate anneals would be for one hour at 650°C. This would provide a stock material with a uniform fine-grained microstructure. Material from the first supply would be cold reduced in a similar way, as a trial. This would be used to confirm that the procedure would be satisfactory and also to devise a straightening process for the annealed 6mm thick sheets.

At the third meeting the supply of replacement material was available and the preliminary work on the first supply had been completed. Specimens prepared from the annealed material to expose surfaces parallel to the rolled surface, perpendicular to the rolled surface and parallel to the rolling direction and perpendicular to both the rolling direction and the rolled surface were examined microscopically. It was confirmed that a fine uniform microstructure had been achieved and that the process used could be used on the stock material for the main part of the work. The only problem in the mechanical part of the work should be straightening of the plates and this would be achieved by stretching by a very small amount in tension. Some reservations concerning detection of segregation of impurities were discussed. Professor Ericsson is confident that Transmission Electron Microscopy will be a satisfactory technique but the possibility that segregates would be preferentially removed in preparing specimens, which would lead to a false negative result could not be discounted. It was agreed that it would be difficult to be confident in a result which showed little or no seggregation owing to the difficulty in examining grain boundaries and the possibility that seggregated material could be removed during specimen preparation. It was also agreed that of the methods available Auger spectroscopy would be tried first.

Separate consultations with UK experts suggest that whilst Auger spectroscopy would work on an intercrystalline fracture surface, such a surface would be very difficult to produce in the microscope. In the absence of such a surface the spatial resolution of the system may be challenged. It was considered that there is no absolutely certain answer, but that Secondary Ion Mass Spectroscopy (SIMS) could be the most favourable method. This technique bombards a surface with a highly focussed beam of Germanium ions which cause secondary ions to be emmitted from the surface. The individual ions are recognised by a time of flight mass spectrometer. The focussing of the beam allows very high spatial resolution.

Work is now proceding, when results from the Auger experiments are available it may be appropriate to consider this alternative.

2.2 Corrosion in the Repository

A series of 5 SKB reports[10-14] on corrosion in the repository have been reviewed and extended critical summaries are provided in sections 8.1 to 8.5. The first of these[10] is a theoretical paper on galvanic corrosion under aerobic conditions corresponding to the period immediately after closure of the repository. It presents the theoretical background to galvanic corrosion and applies it to the case of the canister under aerobic conditions after the copper overpack has been disrupted. It is calculated that under a worst case scenario the rate of corrosion of the carbon steel liner would be 1 mm.year^{-1} and this is similar to the rate of corrosion of carbon steel in seawater. The alternate extreme scenario is also considered. Assuming that the only form of mass transport through the bentonite for oxygen is diffusion, then after several tens of years when a steady state is reached the corrosion rate would be 0.1µm years^{-1}. Both these calculations assume that the areas of iron exposed and the area of copper in contact with bentonite are equal. The writer calculates from the data provided that if the area of iron exposed were 100 cm^2 , which might correspond to accidental damage during placement and backfilling, the expected canister lifes would be 24 days for the worst case scenario and 333 years for the best case.

Considering the best case scenario the original authors point out that the assumption on mass transport is unrealistic. Convection, groundwater flows and temperature gradients will conspire to increase the corrosion rate. The authors believe that the combined effect will be less than a factor of 10^4 increase in the corrosion rate. The presence of chloride in the repository will promote pitting corrosion of the iron. Data presented in the paper have been used by the writer to show that, under pitting conditions and reasonable assumptions on area of pitting, canister life could be in the range 3.5 hours and 40 years. The authors conclude that there is currently insufficient data to make firm predictions of canister life for the case where the overpack is disrupted under aerobic conditions. Earlier work[11] indicates that uniform corrosion of the copper in the repository environment would be negligible over a period of 10^6 years.

A third paper[12] describes an experimental study of anaerobic corrosion corresponding to the period after all the oxygen in the repository has been consumed. The approximate equilibrium corrosion rates of carbon steel (after 5000 hours) in high ionic strength groundwater (pH 10.5) and the bentonite equilibrated high ionic strength groundwaters were 0.7 and 0.1 µm /year. This corresponds to lives of 70,000 and 500,000 years respectively for the two cases. These cases however assume no effects arising from galvanic coupling of the copper and the steel.
Galvanic coupling was examined in a second experiment. The overall conclusion was that galvanic corrosion under aerobic conditions is limited by the low rate of mass transport through the backfill. (The work described in 1 above is referenced to justify this, 1 above refers to an earlier paper by L Verme as it`s justification.). The work concludes that under anaerobic conditions an adherent magnetite film stifles galvanic attack. This indicates that for the case where the copper overpack is disrupted, the security of the system against failure through galvanic attack depends on the whether the disruption occurs in the aerobic or anaerobic phase.

A third experiment is aimed to increase confidence in the assertion that, once formed the magnetite film will afford protection against corrosion for the rest of the target life. The results suggest that after the end of the aerobic phase a magnetite film will form and that it will be protective. It is silent on when or how the aerobic phase will end.

A fourth experiment shows that under anaerobic conditions damage to the magnetite film will be self-healing and its protective function will be restored.

The fourth paper[14] is a thermodynamic study of pure copper corrosion in chloride containing water. It concludes that corrosion of copper due to a high chloride concentration in the bentonite would be negligible over a period of 10^6 years. Other work cited concludes that corrosion involving oxygen or sulphur would be negligible over the same timescale providing that the copper is pure and undamaged.

Taken together these four papers suggest that in the absence of localised corrosion effects or mechanical damage the copper overpack would provide corrosion protection to the canister for its design lifetime and beyond. The absence of or disruption to the copper overpack by any means during the aerobic phase could lead to very rapid failure of the canister. In the anaerobic phase the magnetite film which forms on the steel will provide adequate corrosion resistance. Conclusions from this would be that the copper overpack needs only to be designed to last to the end of the aerobic phase, and that a disrupted copper overpack is worse than no overpack at all. The final paper[13]explores the likely effects on corrosion resistance of changing from a carbon manganese steel to a cast iron for the liner. The compositions of the steel and the iron are given but the metallurgical condition was not determined for either. Specimens were in the form of fine wire. The work concludes that the corrosion rates of the cast iron are considerably lower than the rates for the carbon manganese steel. Since, the carbon manganese steel examined is not similar to the high strength low alloy steel proposed for the liner, and, it is unlikely to be in a similar metallurgical condition to the canister steel, and, the cast iron is unlikely to be in a similar condition to the cast iron of the canister, this conclusion has to be treated with considerable caution. A further study, reported in the same paper, examined hydrogen evolution rates during exposure of carbon steel specimens to synthetic groundwater under anaerobic conditions. It suggests that the oxide film forming on the surface is predominantly magnetite (Fe_3O_4), and that as the film forms, the corrosion rate falls exponentially to less than 0.1µm per year.

2.3 Technology Developments

2.3.1 The Current SKB Programme

At a meeting in April 1997 SKB indicated that it is necessary to have a series of six canisters to use in underground trials at Äspö. It had been decided that these canisters would be made using existing technology. It was recognised that they would not be representative of the final canisters but that their production and use in the Äspö trials will add to the learning on canister production and behaviour as well as enabling the other trials to go ahead.

These canisters would have cast liners and the first six liners produced would be used. It would not therefore be possible to carry out destructive testing of these castings. The overpacks would be fabricated from plate. The plate would be from MKM or Outokompu and it would be 60mm thick. Roll forming of the plate had been done at Kockums (Malmö). Welding of tubulars using the high vacuum vertical EBW process had started at TWI. Tubulars would be subject to NDT and machining at VSEL, lids and bases would be made by forging at Outokompu in Finland in OF copper. Bases would be welded in place at TWI prior to final machining and integration with liners at VSEL. Lids would be attached using mechanical fasteners.

Further meetings with SKB were held at Kockums in April 1997, TWI (Cambridge) in May 1997 and at their offices in Stockholm in December 1997. Information presented in the following sections on technology development was provided by SKB at these meetings.

2.3.2 The Load Bearing Liner

SKB commissioned the first trial casting for the steel liner early in 1996. It was made at full diameter and half-length at the Kolswa foundry. It has been reported earlier that this liner had serious shrinkage defects and that further work would concentrate on development of castings in nodular iron.

The foundry selected for the further work is very experienced in the production of very large castings for paper mill rolls. Such rolls are frequently much larger than the canister which is of concern to SKB and the selected foundry should have no problems with melting and casting capacity. The design of the cast liner is complex however and it will be necessary to demonstrate that defects arising in the casting as a result of feeding difficulties, shrinkage after solidification and cooling rate are acceptable.

It is understood that a simple direct casting approach has been used and that the results are promising. The writer and representatives from SKI are to be invited to visit the foundry and to see the early attempts to make the casting in the future.

Two castings were seen during the visit to Kockums works. There were signs of some shrinkage defects (holes) on the bottom of one but they appeared to be very shallow. The general surface looked very good, one was machined and one was not. Claes Joran Anderson said that there had been a problem of sintering of the sand inside the cores of one casting. He added that this is not unexpected, not serious and that it will be easy to overcome. It was understood that the machining was done at Kockums.

It is understood that the finished casting was nominated I 6 and four further castings, I7 to I11have now been made in nodular iron. Two further inserts, I12 and I 13 are scheduled for production early in 1998. I7 has been cut up for test purposes and feedback on the results is expected from SKB. Visual inspection of sections by SKB representatives did not revealed any defects of serious concern. There is no bond between the steel sections used for cores and the cast iron and there is some distortion of the cores. This is acceptable to SKB who use a template of 150mm square section to test whether or not a fuel bundle will enter the cavity. The fuel bundle has a section which is 140 mm square. The steel components used for cores have a 180mm square section internally.

Eight more inserts, I13 to I20 are scheduled for casting later in 1998. Two of these will be made to accommodate the PWR fuel bundles, which are larger in cross section and may only be accommodated four to a canister.

In order to limit the bending of the core inserts a modification is being made to the casting. It is argued that the bending arises as a result of the slow cooling of the heavy mass of metal in the insert corners compared with the relatively rapid cooling of the narrower structures between the cores. To overcome this SKB propose to include further circular section cores in the heavy corners, these will have the effect of reducing the mass of metal in the corners and, it is argued, thereby cause a more uniform cooling rate which will decrease the tendency to bending of the cores. In addition to controling the bending of cores, such a modification is likely to help in the control of shrinkage defects and of the form of the graphite in the microstructure. On castings of this size in nodular iron it is common practice to employ a post heat treatment to relieve stresses and improve microstructure. SKB have so far not disclosed any plans for work of this kind. Whilst there is a significant cost benefit in avoiding the post heat treatment, it is possible that it may be necessary.

The sealing of the lid to the liner is a matter requiring further clarification. It has been suggested that mechanical fasteners may be preferred to welds, owing to difficulties that may be experienced in welding. It is necessary to decide which method will be used. If it is to be welding, what process and quality assurance procedures will be employed ? If it is to be a mechanical fixing what seals will be used ? How is the durability of the seal to be predicted ?

2.3.3 The Copper Overpack

2.3.3.1 Fabrications

Six copper tubulars have been made from material supplied by Outokompu. They are identified as T6-T11. T6 is in material of thickness 65 mm, T7 is of plate having a thickness of 40 mm and the remainder, are from material of thickness 60 mm. They have been roll formed at Kockums and seam welded at TWI. Two of these will be used for experiments at Äspö and the remainder, are for exhibits and for laboratory work.

Six lids and six bottoms have been made by free form (without the use of closed dies) forging. No details of forging procedures have been given. One lid and one bottom have been welded to a short cylinder for demonstration purposes. The remaining lids and bottoms will be machined in the near future. It was disclosed that tools for closed die forging are to be ordered early in 1998.

Eight further 60 mm thick plates have been delivered to Kockums for roll forming to produce tubulars T12 to T15.

Two copper overpacks were seen at Kockums, they were as delivered from TWI. And they were destined for the Äspö programme, welding defects were clearly visible, they may or may not be removed by the machining process. Kockums were planning to do the machining and they thought that it would not be difficult. If there are problems they believe that they can get good support from Sandvik. It may well be that Sandvik will be asked to give support in controling the machining swarf which tends to be continuous. This is likely to be a considerable problem in production.

The use of 40 mm thick plate on tubular T7 represents a possible concession on the design which would allow the wall thickness of the overpack to be reduced to 30 mm. Fabrication from less thick plate would also be easier than fabrication from the presently favoured 60 mm plate and control of grain size and related problems in the plate would be less difficult. Control of microstructure close to welds and the craft nature of the roll forming process would still make serial production very difficult.

In the light of experience SKB now feel that fabrication from plate is an unsatisfactory process for serial production and that alternatives must be explored (CJA-21 May 1997).

A 30 mm thick overpack would enable a much smaller ingot to be used for extrusion and much higher extrusion ratio to be achieved. The double benefit of this would be that the ingot itself would be much easier to make to a satisfactory quality and it could be much easier to develop a fine-grained microstructure in the extruded tubular. Double benefits would also arise in ultrasonic testing from the lower thickness and from the finer grain size.

2.3.3.2 Extrusions

Six 850 mm diameter x 2.2 M long ingots have been cast by Outokompu for use in trial production of seamless pipes, T16to T21. These were not easy to make and Outokompu did it during their stop weeks. It was explained that the surface quality was not suitable for extrusion trials but it was considered satisfactory for “pierce and draw” trials which will be discussed later under new technology. T16 to T18 are going to be made at Wyman –Gordon in the UK by extrusion and in view of the comments on surface quality of the ingots it is assumed that they will be machined all over before extruding. Earlier trials had developed very coarse grain sizes and the further trials will be made in attempts to produce more favourable structures. T19-T21 are to be made by the pierce and draw process which is described in the next section.

The difficulties in producing suitable ingots for extrusion and in producing suitable microstructures by extrusion coupled with the acceptance that fabrication involving roll forming is an unsatisfactory process for serial production provide a powerfull incentive for SKB to seek to reduce the wall thickness of the overpack or to find an alternative manufacturing process.

2.3.3.3 Alternative Manufacturing Technology for Tubulars.

Three of the 850 mm diameter ingots referred to above will be used to trial an alternative tube making technology offered by the Mannesman company in Germany for tubes T19 to T21. (This technology should not be confused with the well-established Mannesman process for tube making*.

* Metals Handbook-Desk Edition 1995 p1.24

It is a Pierce and Draw process in which the ingot is first upset to destroy the cast structure and then it is pierced and simultaneously drawn through a die to form a tube with a bottom. This is similar to the process used for making cartridge cases or toothpaste tubes but on a much larger scale. In principal it is a very attractive option since it eliminates the seam weld and the bottom weld. If it may be carried out at low enough temperatures to leave residual cold work in the material it provides an opportunity to develop a uniform fine grain size after annealing. In addition machining in the partially cold worked condition will be much easier to perform than it has been on any of the cases which have been examined to date. It will still be difficult to achieve sufficient working of the structure of the material and to make it uniform and to finish at a low enough temperature.

2.3.3.4 Electron Beam Welding

Earlier reports[1,2,3] detailed the problems experienced by TWI in the production of satisfactory welds in fabricated canisters. Some success had been achieved with seam welds but no completely satisfactory lid weld had been made.

TWI were very optimistic that improvements to the welding equipment and the use of inclined welding would produce satisfactory welds.

Early in 1997 lid welds were attempted in which the joint line between the lid and the body of the canister was inclined at angles up to 37.5^{o}. The purpose of this approach was to overcome the problem of pour out of liquid metal from the weld when beam instability arises from whatever cause. Such pour out events cause weld defects which have so far proved to be irreparable.
TWI reported (meeting of 21 May 1997) that the difficulties involved in inclined welding are more severe than the difficulties involved in horizontal welding and that attempts to use that approach have been abandoned.

The electron beam welder for installation in the SKB pilot plant has been ordered and further development work will be carried out after it has been delivered.

At a meeting on 21 May 1997 at TWI when SKI and SKB staff were present, Alan Sanderson (AS) of TWI outlined the principles of the EBW process as they have been applied to the SKB programme and a video tape of a recent welding trial was demonstrated.

AS explained that a benefit of reduced pressure rather than vacuum welding for lids is that it helps accommodate outgassing from the volume between the steel liner and the overpack. It also makes it easier to position the weld on the intended weld line (because the weld is wider). These benefits are in addition to the benefit of avoiding weld root defect which published papers have highlighted. It was pointed out that the price of the benefits detailed above is a wider weld line and coarse grains in the weld region.

He also gave some figures for vacuum levels, the electron gun operates in a vacuum of $5x10^{-6}$ m.bar, the weld region has a higher pressure-possibly 50 m.bar, owing to the Helium shield on the beam and the chamber is held at 0.5 m.bar. When inclined welds are made extreme problems arise as a result of the development of bubbles of vapourised species in the weldpool, for the inclined case the bubbles are large and they burst through the surface of the weldpool energetically (bumping). With horizontal welds the vapourised material does not become trapped as large bubbles and the problem is much less severe. It is for this reason that the inclined welding approach has been abandoned.

Specimens of horizontal seam welds were exhibited and it was pointed out that they had very irregular surfaces that needed to be machined to remove crevices.

The reason given for the use of conical lids was to overcome problems arising owing to expansion of the vessel during welding, this must be additional to the need to control pour out.
A video tape recording of a lid weld being made, showed the instabilities which led to pour out very clearly and the indexing of the tape to the process enables the location of the events observed on the tape to the surface of the weld with precision. Pour out appeared to be preceded by a build of material in the weld pool that had different optical characteristics to the weldpool as it was generally observed.

It was suggested that this effect was a build up of impurities rejected by the melted material as it resolidified, in other words, zone refining.

A further reference to Electron beam welding of copper[17] has been summarised in section 8.7, this work used much lighter sheet than the plate being used by SKB but they also used lower power equipment. They met many of the problems experienced by TWI, in particular the length of weld which could be made successfully seemed to have a limit for specific materials. This is consistant with the suggestion that the effects of Zone refining in the weld pool interrupt the beam stability.

It is clear that considerable further work is needed to develop a satisfactory Electron beam welding process for lids. It will also be necessary to carry out a learning and confidence building exercise in the welding process when its form has been finalised. As well as determining sensitivity to equipment variables it will be necessary to explore process variables and materials variables. This is a considerable exercise, which will include extensive metallographic studies of weldments to ensure that acceptable metallurgical structures are developed.

2.3.3.5 Alternative Welding Technology

A novel welding process, Friction stir Welding, is to be tried for lid welds on the canister. It has been under development for Aluminium at TWI for some time and more recently there have been successful trials on Copper plate of thickness 15 mm. It has the advantage of being a solid state process but, in common with electron beam welding, all the energy input is localised in the region of the weld. In the trial referred to, a Butt weld had been made. A rotating mandrel was inserted in the weld-gap and pressure was applied across the gap whilst the rotating mandrel was traversed in the welding direction. The mandrel caused localised heating, which enabled a pressure weld to be made without heating a large volume of material. Such a process, if it can be made to work on the canister (and there are no obvious reasons why it should not) could enable control of the microstructure in the region of the weld, eliminate any effects of zone refining which may be seen with electron beam welding and eliminate unsoundness which arises following processes involving melting.

2.4 Quality Assurance

2.4.1 Quality Manual

A quality manual has been started by SKB to cover the manufacture of canisters. It is in loose-leaf form as it is a “live” document, which will be subject to regular updating as knowledge develops. It will include all drawings, details of all technical procedures and all technical specifications.

A series of Design Review Meetings have been inaugurated in order that the updating process can be placed on a regular basis and that a quality system may be developed. Quality Audits have started on candidate foundries, for production of inserts.

2.4.2 Non Destructive Evaluation (NDE)

It was previously reported[2,3] that TWI and others were pessimistic concerning the prospect of detecting defects near welds using ultrasound owing to the effects of coarse grains and poor coupling. They were also concerned that digital radiography would miss lines of small pores linked to the surface in the weld regions.

Recent work[8] reported by Posiva (which is summarised in section 8.9) confirms the TWI findings. An exercise designed to optimise the procedures and equipment for ultrasonic testing of lid welds concludes, “ It can be estimated that planar defects having diameter greater than 5mm and located perpendicular to the beam can be detected reliably”. This is a case of damning the process by faint praise.

The current production batch of canisters is being subject to NDE by VSEL. The second tubular from the current batch was seen at TWI. It had been ultrasonically tested and marks close to the weld indicated that through transmission or pitch and catch technique had been used. The marks were typically –10 to –20 dB indicating that the beam had either been steered by coarse grains or it had encountered significant reflectors. Coupled with the comments above this suggests that the welds contained quite significant defects.

It is understood that a contract has been placed for the production of an ultrasonic test system for inspection of welds but the specification of the system has not yet been revealed. Equally no specification has yet emerged for the type and location of defects which need to be detected. It is apparent that conventional ultrasonic systems are unlikely to reliably detect strings of pores linked to the surface which arise from the welding process, or any similar defects. Earlier reports[3] have indicated that eddy current methods may be developed to detect surface breaking cracks but not subsurface defects. Radiography will show some defects but small defects in the weld are missed.
Prof Stepinski at the University of Uppsala has been visited to discus his approach to ultrasonic inspection of canister material, and to present the result of earlier work by Bowyer and Crocker[9].
The earlier work was discussed and particular reference was made to the uncertainty surrounding the effects of annealing twins.

Professor Stepinski recognised the danger of false positives and took notes. He did not promise to take any action but he gave the impression that he would like to investigate it. The Thompson model was discussed and the Bowyer / Crocker implementation was explained, Prof. Stepinski has used a different, statistical model, also with some success. He will now look at the Thompson model bearing in mind the experience discussed. His model had been very successful also, it calculates a probability function for signal levels from the microstructure, it then compares actual signal levels and determines the value of a K parameter to make the probability observed, match with that calculated. The presence of a defect leads to a significant change in the value of K required to make a fit.

Prof. Stepinski has devised an electronic means of signal to noise ratio improvement[15], an SKB report describing this development is summarised in section 8.7. It is a derivative of split spectrum processing. A volume scan is considered in its entirety to determine the frequency contents of the primary signal and the noise. A frequency shift can be measured between the two. Electronic filtering to reduce the frequencies dominating the noise signal leads to a dramatic reduction in noise with no corresponding reduction in signal. He has been given a defect size versus depth in the specimen profile which detection equipment should be designed to meet. I did not ask for a copy of this since it was considered to be more appropriate that it should be supplied by SKB. It was revealed however that it calls for the detection of small defects near to the surface with defects of gradually increasing size as the distance from the surface is increased. (This is the most difficult specification to meet.) He has also devised eddy current methods to detect surface breaking and near surface cracks. Details were not presented but the performance claimed was impressive and would be suitable for detecting cracks arising from hot shortness.

The specimens available to Prof. Stepinski originated at TWI and he claims that they do not have structure noise. The specimens used in the Bowyer / Crocker work were offered and these have now been delivered and it is understood that they will be used to test the signal to noise improvement technology developed at Uppsala.

3 OBSERVATIONS FROM THE MRS MEETING IN DAVOS SEPT/OCT 97

3.1 Canister Technology

There were no papers on materials selection or production technology for canisters. This is surprising, as there is no evidence to suggest that any of the participants have designed and manufactured a suitable canister at this stage. There was a clear impression among participants that the Swedish programme is the most advanced in this respect. Philip Richardson in a keynote presentation said that SKB had made a quality assured canister and (in private) Lawrence Johnson of AECL said that the first choice for the Canadian programme is a Titanium alloy canister and that if this should be infeasible then they would fall back on the technology developed in the Swedish programme.

3.2 Effect of water conductivity on Swelling in Bentonite

The EU supported FEBEX experiment on a simulated full-scale engineered barrier (EBS) system in crystalline rock was extensively reported. Its objectives are to examine the practicalities of manufacturing and placing the EBS components and to evaluate the thermal-hydro-mechanical behaviour in the near field.

Both experimental and modelling studies are included in the programme. For the system considered it is predicted and experimentally confirmed that the first effect in the bentonite is drying close to the canister and this followed by rewetting by entry of moisture from the rock. Drying at a point in the middle of the bentonite barrier was measured after 40-45 days and resaturation was not complete after 3 years. Desaturation of the rock may control the rate of resaturation of the bentonite but it is predicted that resaturation will lead to an increase in swelling stresses in the bentonite.

The Grimsel test facility was visited and discussions were held on the research activities, which have been carried out to date. Of particular interest to the canister problem was work on the damage zone in the rock arising from the tunnelling operations. The fracture zone arises as a result of the mining operations as well as release of the vertical and horizontal stresses in the rock immediately surrounding the excavation. The extent of the damage is related to the intensity of the stresses in the region before mining operations and the direction of mining compared with the direction of stress in the horizontal plane. In the tunnels at the Grimsell test site the vertical stress is equivalent to the pressure from 400 to 500 metres of rock and the peak horizontal stress arising from tectonic pressures may be up to twice or three times this.

Whilst the damage arising from release of vertical stresses is not affected by the horizontal component of the tunnel direction, that arising from the release of horizontal stresses, is maximised when the mining direction is perpendicular to the direction of the maximum stress and minimised when it is parallel to the direction of maximum stress.

The relevance of this to the Swedish Programme is that when a vertical hole is bored in the floor of the tunnel we might expect that the fracture pattern in the rock around the bored hole will vary around the hole, being most severe in the direction perpendicular to the maximum stress and least severe in the direction parallel to the maximum stress.

This may be important from the point of view of hydrological conductivity since fractured rock has increased conductivity compared with the rock which is undamaged by the process of excavation. Also conductivity in undamaged material is strongly influenced by the natural discontinuities and is therefore inhomogeneous. The effect of a uniform fracture zone around the excavation would reduce any effects of this inhomogeneity as well as increasing conductivity. In the case where bentonite is absorbing water from the host rock, a uniformly fractured rock will improve the uniformity in the rate of supply of water to, and therefore the swelling stresses in the bentonite. Non uniform stresses in the bentonite could lead to flow of the copper overpack and lead to local reductions in thickness. Bearing in mind the extreme lack of creep resistance of the selected overpack material and the very long timescales under consideration, such reductions in thickness could be severe enough to cause concern.

Canisters deposited in horizontally drilled holes in suitable orientations would of course be much less susceptible to this problem.

Whilst controlled wetting of the bentonite immediately after emplacement can help the initial swelling to be uniform it is necessary to understand the variations which will arise in the swelling stresses as the water in the Bentonite – Rock – Canister system approaches equilibrium.

3.3 Workshop on microbial effects

This was a workshop lead by P Humphries of BNFL and J M West of the British Geological Survey. Both made the point that, whilst knowledge on the effects of microbes is limited, all experiments which have been carried out have been in the presence of microbes and the results have therefore been affected. There is difficulty recognising the microbial species that will be present in any environment or how they may mutate in response to an environmental challenge.

A suggested approach to overcome this difficulty was to use modelling which does not specify the species but which assumes that activity will continue until all nutrients are used. This approach defines the functional groups in the metabolism of the microbe rather than the microbe itself. There was concern expressed that even if the total amount of microbial activity is limited, localisation of effects may lead to significant damage. There was general agreement that the presence of the radiation field and the elevated temperature were unlikely to limit microbial activity in the long term. There was no specific knowledge on the effects of microbial activity on copper and there was agreement that there is a need for a serious investigation of the effects of microbes in the repository environment. It was considered that the need for long term work had inhibited the flow of funds required to make substantial progress.

4. DEFECTS IN O.F. COPPER

A search to identify the nature and causes of defects in OF copper has been continued throughout the year. Results of, consultations with the UK industry and with the Copper development association and searches of the UK and US CDA archives have been disappointing. Indications are that the information, which may be relevant to canister production, was mainly collected more than thirty years ago and archives either do not exist or are not accessible. Some of the people who were involved in studies during the 1950 to 1970 period have been contacted but they have been unable to help with other than anecdotal information. It must be concluded that information on the defects likely to occur during the manufacture of the copper canister is not freely available in written form. It will be necessary in the later stages of development and early stages of production to collect and document such information.

5. THE FINNISH PROGRAMME

STUK is the Finnish equivalent of SKI and SSI and a meeting was held between SKI and STUK staff to exchange experiences and consider ways of co-operation in the future. My reason for being present was to listen to and comment on their experience in relation to the canister.
Esko Ruokola described canister development and it was clear that the Finnish work is at a very early stage. The Finnish concept is very similar to the Swedish concept and seems to be moving in the same way even though they have done very limited experimental work. For instance they are considering a nodular iron rather than a steel liner, and it will be cast in a similar way to the Swedish liner. The decision to use cast iron in the Swedish plan is quite recent and only limited work on this concept has been done in Sweden. One difference to the Swedish design is the provision of cylindrical cavities in some liners rather than the rectangular section cavities, this is to accommodate different shaped fuel packages from one of their reactors. If the impression that they are following the Swedish programme at a respectable distance is accurate then they will have to do some independent development work to accommodate this different cavity design. There is a fundamental weakness in the strategy of following at a so called safe distance however in that, the Swedish engineers will experience a learning in their development process which will help them understand the sensitivity of the process to manufacturing variables. This knowledge is not easily available to the one who copies only the end result.

It was said that the cast iron liner would also have a cast iron lid but it was not said how it would be attached.

Work by Posiva (the Finnish equivalent of SKB) on the copper canister was referred to, the concept appears to be identical to the Swedish concept. STUK have the impression that canisters will be made by roll forming and welding. They did not appear to be aware of the difficulties experienced by SKB in welding lids or that different welding processes are used for the lid and the seam welds. Welding research has been done both in Finland and in Germany. The work in Finland was done by FIN ABITECH an aviation company. In response to my surprise that an aircraft company would have the capability to make these welds it transpired that they had done feasibility trials on relatively thin material. Such work would show that thin copper plate can be satisfactorily welded but it would not address the difficulties of welding heavy plate which are being experienced by SKB. We were not told who had been doing trials in Germany but the information may be available from Posiva.

STUK understood that no cylindrical specimens had been made and that all trials had been performed on flat specimens. However specimen lids had been made by forging and they were fine grained, this is interesting since we have so far seen no evidence that SKB have achieved fine grain sizes in forged lids.

STUK also felt that some of the ultrasonic testing problems had been solved and that creep tests on specimen welds indicate that they will have satisfactory creep strength.

The forward programme for Posiva is to select a manufacturer and manufacture a demonstration canister by mid 1998, to scale up to a full size canister in 1999, to develop QA procedures in 1999 and to complete a plan for an encapsulation plant by the end of 1998.

The research budget for 1998 was a total of 8million Fin Marks; it was assumed that this is the budget available to STUK and that Posiva have a considerably larger budget.

Two Posiva reports were provided, one on ultrasonic inspection of EB welds and one on creep performance of EB welds. These are summarised with comments in sections 8.9 and 8.10 and have
already been referred to in sections 2.1.2 and 2.3.3.4.

6. CONCLUSIONS

6.1 Liner Materials

Cast steel has been rejected as a candidate for the load bearing liner in the copper iron canister owing to problems arising from it`s shrinkage caharacteristics.

Nodular (or Ductile) cast iron, which is being examined as an alternative, could match the mechanical strength characteristics of the high strength low alloy steel which was originally specified for the component, providing casting conditions and composition can be adequately controlled. There will be a penalty in ductility, which will be reduced from 25-30% to a value between 1 and 18% depending on control of casting conditions.

It will be necessary to determine and specify the precise composition and casting practice for the selected iron to obtain satisfactory and reproducible properties. This is usually done through examination of a series of trial castings in a development programme. In the programme the effects of composition and casting practice on soundness and metallurgical structure/ properties will need to be explored.

6.2 Overpack materials

The material specified for the copper overpacks at present is OF copper with 50 ppm of phosphorus added. This specification and the manufacturing procedures for the overpack are under review. It is not until acceptable manufacturing procedures are defined that the specification of the material can be finalised.

It is recognised that levels of residual elements will need to be controlled below the levels in the OF specification. This is not difficult but it is not certain that key elements such as sulphur can be controlled to a low enough level and increasing purity will lead to increasing processing difficulty.

The question of low creep ductility in coarse-grained material with 7 ppm sulphur has not been resolved.

A suggested reduction in the thickness of the overpack to 30 mm would reduce manufacturing problems somewhat and should enable much better control of the microstructure. The effect of such a reduction on the shielding performance of the canister has not been published.

A short research exercise funded by SKI will examine the recrystallisation characteristics of the stock material currently used in SKB trials and also examine the seggregation of impurities to grain boundaries as a function of grain size.

6.3 Corrosion

A study of SKB reports suggests that in the absence of localised corrosion effects or mechanical damage the copper overpack would provide corrosion protection to the canister for its design lifetime and beyond.

The absence of or disruption to the copper overpack by any means during the aerobic phase could lead to very rapid failure of the canister. In the anaerobic phase the magnetite film which forms on a steel would provide adequate corrosion resistance following disruption of the overpack if the liner was of a similar steel.

Under anaerobic conditions damage to such a magnetite film would be self-healing and it`s protective function would be restored.

The change from a steel liner to a cast iron liner could change the nature of the magnetite film forming on the liner. The work designed to test this is not reliable owing to the failure to match the structure in the experimental material to that expected in the liner.

The duration of the aerobic phase in the repository is uncertain. SKB contractors consider that, to assume that availability of oxygen is limited by mass transport through the bentonite is unrealistic, owing to the effects of groundwater flows.

Possible mechanisms for disruption of the overpack include, damage during emplacement, localised corrosion, creep failure during the collapse of the overpack onto the liner and longer term creep failure owing to uneven pressures due to swelling of the bentonite.

6.4 Technology Developments-Liners

Several full size cast iron liners have been made. One is being subject to quality checks the remainders are to be used for trials in the Äspö hard rock laboratory.

The finished dimensions of the cast liners are satisfactory and current development is concentrated improvement to the casting design.

The means of attaching the lid to the liner has not been disclosed. The hermetic seal originally planned for the fabricated steel canister will be equally difficult to achieve for the cast iron case.

6.5 Technology Developments-Overpacks

A number of overpacks have been fabricated using roll formed tubulars and forged bases. These are for experimental purposes and are not expected to meet quality standards in the material or the welds. Bases will be welded in place and lids will be fixed mechanically.

It is now considered by SKB that fabrication of the overpack by roll forming is an unsatisfactory process and an alternative is being sought.

The alternative manufacturing methods under consideration are a pierce and draw process operated by Mannesman and extrusion. These may be tried with 60mm or 30 mm wall thickness. Neither of these processes is developed for the proposed application.

The attempts to resolve difficulties with welding lids onto the overpack by using an angled beam have failed. Future development of the welding procedure will await the commissioning of the pilot plant in Sweden.

An alternative welding process “Friction stir welding” is in the very early stages of development.

6.6 Quality Assurance

Existing ultrasonic methods are not capable of reliably detecting small defects which occur in the welds on the overpack. Improved methods are under development but considerable further development is needed.

Eddy current methods are likely to be capable of detecting surface cracks arising from hot and cold shortness.

6.7 Manufacturing

Kockums have been identified as a Swedish organisation for carrying out many of the canister fabrication activities.

Information on the origin and consequences of defects in copper used for the canister is not available in published form and it will be necessary to develop this knowledge during the development programme.

6.8 Effects of the Repository Environment

Non uniform swelling in the bentonite can arise from variations in water conductivity in the fractured rock around deposition holes. It is necessary to determine whether or not this is likely to cause failure of the overpack by creep.

Knowledge on the effects of microbes in the repository on the canister is very limited, there is a view that long term research is required to assess the risk which it could present.

6.9 The Finnish Development Programme

The Finnish programme on waste disposal is very similar to the Swedish programme but some years behind. Timescales set for meeting development targets suggest a lack of appreciation of the problems involved.

7 REFERENCES

1. W H Bowyer, Design Basis for the Copper /Steel Canister, Stage Two .Final Report . SKI Report 96:47 February 1996
2. W H Bowyer and H P Hermansson, Comments on “SKB FUD Program 95” Focussed on Canister Integrity and Corrosion, SKI Report 96:42, March 1995
3. W H Bowyer, Design Basis for the Copper /Steel Canister, Stage Three. Final Report . SKI Report 97:19 February 1997
4. P Auerkari and S Holmström, Long term strength of EB welds of the canister for nuclear fuel disposal. Posiva Working Report-97-35e, September 1997
5. M Owen , IMI Refiners Limited-Private Communication October 1996
6. I Campbell, Outokumpu (UK) Limited, Private Communication February 1997
7. BS Draft for Public Comment, Document Number 95/708881, June 1995
8. H Jeskanen and P Kaupinnen, Ultrasonic inspection of electron beam welded joints in copper. Posiva Working Report-97-34e August 1997
9. W H Bowyer and RL Crocker. Modelling attenuation and scattering of ultrasound in polycrystalline copper. SKI report to be published, April 1997.
10. D J Blackwood et al The effect of galvanic coupling between the copper outer canister and the carbon steel inner canister on the corrosion resistance of the Advanced Cold Process Canister. SKB Project report 95-04 August 1994
11. D J Blackwood et al. Further research on corrosion aspects of the Cold Process Canister. SKB Project Report 95-05 August 1994
12. D J Blackwood et al., The anaerobic corrosion of carbon steel in granitic groundwaters. SKB Project report 95-03 February 1995.
13. N Smart et al., Corrosion aspects of the copper-steel/iron process canister: Consequences of changing the material for the inner container from carbon steel to cast iron. SKB Project report 97-04 June 1997.
14. C Taxén, Corrosion of copper in chloride containing waters, A thermodynamic study. SKB Project report 94-02 September 1990.
15. A Sanderson et al., The application of high power non-vacuum EB welding for encapsulation of nuclear waste at reduced pressure,-Summary report. SKB Project report 94-01
16. T Stepinski Inspection of copper canisters for spent nuclear fuel by means of ultrasonic array system. SKB Project report 97-06 August 1997
17. MS Bingley and DW Davis –Electron beam welding copperand dilute copper alloys BNF Report 608/7

8 EXTENDED SUMMARIES OF R&D REPORTS

8.1 D J Blackwood et al The effect of galvanic coupling between the copper outer canister and the carbon steel inner canister on the corrosion resistance of the Advanced Cold Process Canister. SKB Project report 95-04 August 1994

This paper gives the theoretical background to galvanic corrosion and applies to the problem of the canister in the repository after the overpack has been disrupted.

For the case where the copper carbon steel couple corrodes under aerobic conditions standard electrode potentials of iron and copper show that on coupling the carbon steel is expected to become anode and the copper to become cathode. All the cathodic current generated (by reduction of oxygen) at both electrodes will be available to promote corrosion of the steel.
It is assumed for the purpose of conservative calculations that the oxygen reduction reaction is purely under mass transport control and therefore the maximum possible cathodic current is provided and the maximum corrosion rate results. If mass transport is solely by diffusion and planar geometry is assumed (1M diameter), the maximum galvanic current $i_{\max}$, which may flow
across the couple is given by;

$$i_{\max} = \frac{4FDC_0}{\mathrm{d}}$$

Where D is the diffusion coefficient for dissolved oxygen in the conductive solution (groundwater for the real case), C_0 is the bulk concentration of dissolved oxygen, δ is the diffusion layer thickness outside which the oxygen content remains at a constant level (i.e. C_0) and F is Faradays constant.
For the case of an aqueous solution exposed to normal atmospheric conditions:

$D \approx 10^{-5} cm^2 \sec^{-1}$ $\quad$ $C_0 \approx 8ppm(2.5x10^{-7} mol.cm^{-3})$ $\quad$ $\mathrm{d} = 10^{-2} cm$

Therefore,

$i_{\max} \approx 9.6x10^{-5} Acm^{-2}$

The authors state that this is sufficient to maintain a corrosion rate on the steel of 1 mm.year^{-1}.

They further state that the granitic groundwaters expected by SKB to be in the repository groundwater are of similar composition to seawater. Studies on the galvanic coupling of copper to steel in seawater environments quoted by the authors have generally concentrated on 1:1 anode: cathode area ratios. Under these conditions the corrosion rate of steel in seawater has typically been observed to be 0.5 mm.year^{-1}, which the authors point out is reasonably close to the value of 1mm.year^{-1} calculated above which, they suggest, corresponds to the worst case scenario.

It also corresponds to a time to penetration of 50 to 100 years. The calculations and the experiments both refer to the case where anode and cathode areas are equal. The effect of anode and cathode areas will be referred to later.

The alternate extreme considered by the authors is the case where the ACPC is surrounded by a layer of bentonite of thickness 0.5 m, at a pressure of 10 Atmospheres, and in which the only form of mass transport is diffusion. The values of the parameters in the equation for i_{max} now become:

$C_0 \approx 40 ppm(1.3x10^{-6} mol.cm^{-3})$ $\quad$ $\mathrm{d} = 50cm$

$D \approx 10^{-6} cm^2 \sec^{-1}$

Therefore the maximum steady state current that the copper can now supply is approximately $1.0\text{x}10^{-8}$ A cm^{-2}, which is sufficient to cause the carbon steel to corrode at the rate of $0.1\mu\text{m.year}^{-1}$ when anode and cathode area are equal**.** This corresponds to a time to penetration of 500,000 years. This calculation is dominated by the assumption of the value of 50cm (the bentonite thickness) for δ. Whilst the value of 10 Atmospheres for the pressure in the repository may be disputed it`s combined effect on D and C_o is relatively small. The key assumption (δ=50cm), requires that the only form of mass transport through through the bentonite is diffusion. The authors state that calculation has shown that this ideal steady state could not be achieved for several tens of years. (It should also be pointed out that the surface area of the canister is approximately 15 m^2. An exposed area of 100 cm^2 would result in an anode to cathode area ratio of 1500, this would correspond to a life of 12 to 24 days on the worst case scenario or 333 years on the alternate extreme.)

During the period before the steady state could be achieved, the authors state that the galvanic current I_g would be governed by the Cottrell equation:

$$i_g = -\frac{4FD^{\frac{1}{2}}Co}{\pi^{\frac{1}{2}}t^{\frac{1}{2}}}$$

By the authors calculation this leads to a value for i_g of $5.0\text{x}10^{-8}$ Acm^{-1} after 1 year and this corresponds to a corrosion rate of 0.5 μmyear^{-1} for equal areas of anode and cathode. They go on to say that this indicates that, where diffusion is the only form of mass transport in the bentonite, galvanic coupling will not play a significant role in the life expectancy of an ACPC unless the area ratio of the copper:carbon steel is >1000:1. The writer believes that this statement should be viewed with considerable caution for the following reasons.

1. The Cottrell equation carries the square root of time in it`s denominator, thus if the rate is 0.5 µm year^{-1} after 1 year, it will be 2.5 μmyear^{-1} after 5 years and 5 μmyear^{-1} after 100 years, for equal areas of anode and cathode.

2. If the copper layer is disrupted, it is most likely that the area of iron exposed will be small, for the ratio of 1000:1 referred to by the authors the area of iron exposed would be 150 cm^2. This would limit the life to 20 years at the 10-year rate or 10 years at the one hundred-year rate. Using the 100 cm^2 exposed iron these reduce to 13 years and 7 years respectively.

The authors point out that in practice the mass transport of oxygen through the bentonite will probably not be limited to just diffusion. The effects of convection, natural flows of groundwater through surrounding bedrock and temperature gradients will conspire to reduce the value of δ and increase the value of the galvanic current and the corrosion rate. They accept that there is currently insufficient data to predict the likely rate of convection of oxygen through the bentonite to the container. They believe that it is unlikely that the rate will reduce the effective value of δ below the value used in the earlier worst case scenario. A further uncertainty surrounds the effect of pH in the bentonite. The expected pH is 10.5, at this level the authors state that whilst this would not increase the general corrosion rate it could increase the probability of localised corrosion.

A further complication pointed by the authors is that the groundwaters in the repository are expected to contain up to 20,000 ppm of chloride ion. Chloride causes pitting corrosion of iron under aerobic conditions and the copper-iron system will therefore be susceptible to pitting corrosion. Assuming that the oxygen reduction reaction is under mass transfer control on both the copper and steel surfaces, once pitting is initiated, the remaining area of carbon steel will combine with the copper to form an extended cathode. Under these circumstances the galvanically coupled copper behaves as a region of non-corroding steel. The diffusion of oxygen to the surface of the copper and the area of non-corroding steel would then govern the maximum rate of corrosion.

the penetration rate $P_{\max}$ would then be given by;

$$P_{\max} = 11{,}900\left(\frac{4FA_1DC_0}{A_2\mathrm{d}} \right)$$

Where A_1 is the total surface area of all areas suffering localised corrosion, A_2 is the combined area of the copper/carbon steel cathode and 11,900 is a constant to convert current density from Acm^{-2} to corrosion rate in mm years^{-1}. For this scenario the authors calculate that when A_1/A_2 is 500 the time for penetration would be 40 years. The writer urges that this conclusion should also be treated with caution for the following reasons.

1 The authors at an earlier stage have pointed out that the mass transport of oxygen through the bentonite will probably not be limited to just diffusion. The effects of convection, natural flows of groundwater through surrounding bedrock and temperature gradients will conspire to reduce the value of δ and increase the value of the galvanic current and the corrosion rate. They believe that it is unlikely that the rate will reduce the effective value of δ below the value used in the earlier worst case scenario. The effect of reverting to the earlier value of δ would be to increase the corrosion rate by a factor of 10^4.

2 The selected value of A_1/A_2 is quite low and corresponds to a total pit area of 300 cm^2. A more likely area of 30 cm^2 would increase the corrosion rate by a further factor of 10.

3 Combining the effects of 1 and 2 above leads to a penetration time of 3.5 hours. The level of uncertainty that arises from the manipulation of the assumptions within a reasonable range therefore lies between 3.5 hours and 40 years.

The authors conclude that there is currently insufficient data to make firm predictions of canister life for the case where the overpack is disrupted and aerobic conditions exist in the repository.

8.2 D J Blackwood et al. Further research on corrosion aspects of the Cold Process Canister. SKB Project Report 95-05 August 1994

One concern regarding the use of the Advanced Cold Process canister (ACPC) is that in the event of the copper overpack being penetrated; the anaerobic corrosion of carbon steel may result in the formation of hydrogen gas bubbles. Such bubbles could disrupt the backfill leading to increased water flows and flux of radionucleides into the host rock.

SKB Technical Report 92-26 1992 (L Verme) is quoted to support the assertion that " in time, the corrosion of the copper canister will consume all the oxygen which the mass transport processes are capable of delivering to the ACPC". Four research tasks are reported.

The first was motivated by the observation that the ionic strength of the Äspö groundwater (which appears to be used as a standard for the repository case) is much higher than had previously considered. It had also been suggested that the bentonite backfill would dominate the water chemistry for 100,000 years. A key effect of this is that the pH of the groundwater would be adjusted upwards from 8 to 10.5. It was considered necessary to check the effects of these changes in chemistry of the groundwater on the corrosion rate and therefore the rate of hydrogen evolution.

In all experiments the rate of hydrogen evolution fell to equilibrium rate over 5000 hours and this was related to the formation of an adherent magnetite film. This equilibrium rate was five times higher in the high ionic strength groundwater than it was in the previously measured low ionic strength groundwater, which had a pH of 8 or less.

The bentonite equilibrated groundwater of high ionic strength maintained a pH close to 10.5. Experiments in this medium revealed that the long term hydrogen production rate was significantly less than the rate in non-bentonite equilibrated groundwater of the same ionic strength and was the same, within experimental error, as the rate measured for dilute groundwaters.

The authors argue that whilst the high ionic strength can significantly increase the rate of hydrogen production, this is more than offset by the bufferring effect of equilibration with bentonite.

The approximate equilibrium corrosion rates (after 5000 hours) in the high ionic strength groundwater and the bentonite equilibrated high ionic strength groundwaters were 0.7 and 0.1 µm /year. This corresponds to lives of 70,000 and 500,000 years respectively for the two cases. These cases however assume anaerobic conditions and no effects arising from galvanic coupling of the copper and the steel in the practical case.

In a second task reported as part of the same exercise the author considers the effect of galvanic coupling between the copper and steel cylinders in both the aerobic and anaerobic stages of the canister life.

The effects of coupling between copper and the steel during the aerobic stage were not examined, but previous work was referred to (AEA Technology Report, AEA-

ESD-0053, 1994.). It is stated that a main conclusion of this report was that the low rate of mass transport through the backfill would prevent significant galvanic attack of the ACPC.

Experiments were carried out in which hydrogen evolution rates from carbon steel and carbon steel coupled (by welding) to an equal surface area of copper in anaerobic dilute granitic groundwater. At no time during the experiments (duration 5000 hours) did the coupling between iron and copper lead to an increase in the rate of hydrogen production. The authors, in their interpretation, point out that in the short term, before the magnetite layer is established on the steel, this result is to be expected from a consideration of the electrochemical constants. In the longer term, after the magnetite layer is established, the observations indicate that the corrosion reaction is not cathodically limited and therefore the magnetite acts as a true passive film which stops the groundwater coming directly into contact with the steel and stifles the anodic dissolution reaction.

The overall conclusion at this stage is that galvanic corrosion under aerobic conditions is limited by the low rate of mass transport through the backfill and that under anaerobic conditions the adherent magnetite film stifles galvanic attack. This indicates that for the case where the copper overpack is disrupted, the security of the system against failure through galvanic attack depends on the duration of the aerobic phase. The writer points out that in the case examined equal areas of copper and steel were used. It is important to ask whether the same result would be obtained if the area of the anode (iron) were small compared with the area of the cathode (copper) during the aerobic phase.

A third task is consideration of the role of the magnetite film as protection to the steel cylinder. The model used for hydrogen gas generation assumes that the magnetite film forms very early in the exposure life of the ACPC and that it affords protection against corrosion for the remainder of the service life. The task aims to increase confidence in this assumption.
Experiments were conducted in which open circuit potentials of carbon steel electrodes, with and without magnetite films, were measured indirectly against standard calomel electrodes (SCE). This involved carrying out the experiment in artificial anaerobic granitic groundwater at pH 8.1, at both 20^0 C and 50^0C and making corrections for the effect of groundwater, compared with pure water, on the reference electrode potential.

Open circuit potentials were more negative at the higher temperature, indicating higher corrosion rates at 50^0C for both coated and uncoated specimens. Initially, uncoated specimens had higher open circuit potentials than coated specimens but after 700 hours, magnetite layers had formed on the originally uncoated samples and their open circuit potentials had converged to those of the originally coated samples. The open circuit potentials in the steady state were more negative than water reduction potentials at pH 8.1.

It is argued by the authors that a positive shift in the open circuit potential at a time when corrosion rate (hydrogen evolution) is reduced is characteristic of an anodically controlled reaction. This suggests that the oxide film anodically limits the corrosion.

This conclusion was reinforced by potentiostatic measurements, which suggested that the rate-controlling step was transport of Fe^{2+}ions through the magnetite layer. The authors point out that this observation suggests that the magnetite film passivates the surface and that the ratio of anode area to cathode area is of no consequence to the anaerobic corrosion case. The writer concludes that it does not demonstrate that the magnetite film forms very early in the canister life because it does not form until anaerobic conditions are established.

A fourth task investigates the character of the magnetite layer to explore its adherence to the substrate and consequently it`s long term reliability. It was demonstrated that the film which forms under anaerobic conditions consists of two layers, a hard electrochemically produced inner layer of Fe_3O_4 which is tightly adherent and a precipitated outer layer. Damage to the layer is healed during subsequent exposure under anaerobic conditions. It is concluded that under anaerobic conditions the magnetite layer provides the steel examined with robust protection against rapid corrosion.

The hydrogen evolution experiments described for the first three tasks used carbon manganese steel wires of undisclosed composition or metallurgical condition. The carbon manganese steel is not the same as the Cr,Mo,V steel which had been proposed for the steel liner and it`s metallurgical condition is not specified.
This is particularly relevant when mechanisms such as protection by adherent oxide layers are involved, since such layers are likely to be epitaxial.

8.3 Smart et al., Corrosion aspects of the copper-steel/iron process canister: Consequences of changing the material for the inner container fromcarbon steel to cast iron. SKB project report 97-04 June 1997.

This work is focussed on predicting the corrosion behaviour of the steel or iron container in the event of the copper overpack being breached early in it`s service life. It is specifically directed to measurements of hydrogen generation rates from anaerobic corrosion of carbon steel and cast iron in simulated groundwater equivalent to Äspö KAS-03, and in the same water after equilibration with bentonite.

It is stated that one of the reasons for the choice of copper as the overpack is that it should, on thermodynamic grounds, be immune to corrosion in anaerobic aqueous solutions under moderately alkaline (pH <13) conditions. Such conditions are expected to develop in the repository shortly after it has been sealed and saturated with groundwater. A series of 8 earlier reports from AEA (Harwell) relating to corrosion of the carbon steel liner are referred to. These include SKB reports 95-04 and 96-05, which refer to, galvanic coupling between the outer copper and inner steel containers, and Stress corrosion cracking of the steel container respectively and a further report, Blackwood DJ 1996, Corrosion processes on the Advanced Cold Process Canister. A summary of Recent Reports 1996 is also referred to. Earlier work referred to has shown that carbon steel under the specified conditions at $50°^{\circ}$ C will initially corrode at 10µm/year (50mm in 5000 years), however this rate reduces by a factor of 10 after a few months due to the formation of an adherent magnetite layer.

Cast iron contains elemental carbon particles. It is suggested that since carbon is an excellent hydrogen evolution electrode and there is a possibility of galvanic coupling between the ferrite matrix and the graphite, this could lead to an increase in the rate of corrosion compared with carbon steel.

The work compared hydrogen evolution rates from specimens of a 0.2 % Carbon 0.7 % Manganese steel with rates from a 3.7 % Carbon, 0.03 % Nickel cast iron.

The observations indicate; (1) that for the test materials in the test conditions and at 50°C, the long term anaerobic corrosion rates of cast iron in both artificial Äspö KAS-03 groundwater and the same water equilibrated with bentonite, were approximately five times lower than those for carbon steel under the same conditions. (2) that the long-term corrosion rates of both materials were ten times lower in Äspö KAS-03 groundwater equilibrated with bentonite than in untreated Äspö KAS-03 groundwater. and (3) At 85°C the long-term corrosion rates of both materials in untreated water were similar to the rates measured at 50°C.

It is suggested that the long-term rate is controlled by diffusion through an adherent magnetite layer and that this process is not strongly sensitive to changes in temperature in the range examined.

The writer’s comments on this work are as follows:

The carbon manganese steel is not the same as the steel, which had been proposed for the steel liner, and its metallurgical condition is not specified. Since it was in the form of fine wire it is likely that it was in the hard drawn or the annealed condition, neither condition would provide a structure similar to that proposed for the canister. The metallurgical structure of the cast iron was not investigated but it is stated that it would be likely to contain graphite particles in a ferrite or pearlite matrix. This is true but it is inappropriate to assume that any structure in that spectrum would have the same corrosion properties as the nodular iron proposed for the canister. Whilst the composition of the selected material is typical of nodular iron, the cooling rates associated with casting of fine wires is not not conducive to the development of the nodular structure in the graphite or the ferrite structure in the matrix. Galvanic coupling between flake or nodular graphite and ferrite, pearlite or martensite will differ. The failure to investigate the structure of the experimental materials and to match them to the structures of the candidate materials proposed for the canister leaves considerable doubt regarding the relevance of the information provided to the case under consideration.

8.3 D J Blackwood et al., The anaerobic corrosion of carbon steel in granitic groundwaters. SKB Project report 95-03 February 1995.

The writers refer to work in Switzerland, Germany, Belgium, UK and the USA, in which the corrosion allowance required for a 500 to 1000 year life for a steel vessel, in granitic, agrillacious and basaltic formations would be of the order of 50 to 200 mm. There is some uncertainty concerning the hydrogen gas which may be produced by the anaerobic corrosion of iron however;

$$Fe + 2H_2O \Rightarrow Fe(OH)_2 + H_2 \uparrow$$

Mass transport calculations have shown that, if movement of hydrogen away from the canister occurs purely by diffusion in the water which fills the pore space in the bentonite backfill, then at, what the authors refer to as, modest corrosion rates of

10µm per year, the hydrogen activity at the surface will eventually exceed the hydrostatic pressure in the repository. The resultant gas bubbles could cause disruption of the backfill, which could accelerate nuclide transport.

Some of the earlier work involving one of the authors (and refered to above) had taken the conservative view that solid corrosion products confer no protection to the metal surface. Under these conditions the overall corrosion reaction would be under activation control. Consideration of the rate equations with experimentally determined parameters, led to an estimated corrosion rate under anaerobic conditions at 90°C, of 163 µm per year. The corresponding rate at 25°C was 26µm per year (much higher than the 10µm per year referred to above). However the experimentally determined electrochemical parameters for this work were measured in argon purged solutions with negligible hydrogen activity. It is argued that in the practical case a build up of hydrogen could reduce the rates of both the cathodic and anodic reactions through its effects on these parameters. This would have a self-regulating effect on the corrosion rate. One purpose of the programme described was to measure the effects of hydrogen overpressures on the electrochemical parameters.

The second purpose of the work was to investigate the effects of the assumption that the reactions would be under activation control. It is argued that the much lower than predicted corrosion rates, that have been measured in other work (<1 to 20µm per year), are likely to be a result of the corrosion products providing a protective layer on the surface.

A literature survey conducted by the same authors suggests that a steady state develops at which the rate of metal dissolution may be controlled by the rate of dissolution and diffusion of metal ions at and away from the oxide-electrolyte boundary. Thus in the absence of dissolution , film thickening will decrease with time to a negligible rate. The experimental programme was designed (1) to determine the nature of the oxide films formed on carbon steel in granitic groundwater and whether or not subsequent dissolution of the metal is controlled by diffusion away from the oxide –electrolyte boundary and (2) to determine that ,under low diffusion conditions, the rate of film growth falls to negligible levels.

The first experiments (to determine the effects of hydrogen overpressure on corrosion rate) were carried out in synthetic groundwater and 3.5% NaCl solution. The results were not as expected. Increasing the hydrogen overpressure to 10 Atmospheres consistently led to an increase in corrosion rate by a factor of between 2 and 10. In view of the uncertainties in the experiments and their interpretation, the authors conclude that corrosion rates appeared to be almost independent of hydrogen overpressure in the range studied (1-100 Atmospheres).

Gas evolution experiments were conducted on carbon steel wires exposed to artificial groundwater under anaerobic conditions. The rates of gas evolution were used to calculate oxidation rates. Wires in pickled (to remove oxide) and degreased conditions were compared in tests at 30ºC and 50ºC. Results on degreased samples were similar at both temperatures. Initial evolution rates on pickled samples were higher than on degreased samples and and were higher at 50ºC than at 30ºC.

The hydrogen evolution rate fell to a very low level on all specimens after 2000 to 4000 hours. It was concluded that the initial anaerobic corrosion rate on clean surfaces was of order 10µm per year but as the oxide forms this decreases exponentially to a rate of 0.1µm per year. Longer-term (4-year) corrosion tests on coupon specimens in granitic groundwater at 90ºC were in reasonable agreement with the hydrogen evolution results.

The oxide film was predominantly magnetite (Fe_3O_4) and it was concluded that this controlled the corrosion rate and the gas evolution to the relatively low levels observed. No conclusion was drawn on the precise mechanism of protection offerred by the oxide film.

8.5 C Taxén, Corrosion of copper in Chloride containing waters, A thermodynamic study. SKB Project report 94-02 September 1990.

A thermodynamic study of pure copper corrosion in waters containing chloride ions. It is concerned only with copper and its chloride complexes and with protons as the sole oxidising agent. The analysis indicates that the corrosion of copper due to a high chloride concentration the bentonite would be negligible over a period of 10^6 years. Figures from other work indicate that corrosion involving oxygen and sulphur could be 50 to 500 times more severe than corrosion involving chloride and that both would be negligible over the 10^6 years timescale. The work suggests that the copper overpack would offer complete and guaranteed protection against corrosion providing that it was pure, in a metallurgically stable condition and in the specified environment.

8.6 A Sanderson et al., The application of high power non-vacuum EB welding for encapsulation of nuclear waste at reduced pressure,-Summary report. SKB Project report 94-01

This is a summary report on development activities at TWI directed to the welding of the copper canister lids and seams. It covers two years work to November 1993. It provides detailed results on experiments in the development programme. The results and conclusions presented have been repeated or superceded in later reports which have been discussed previously[1].

8.7 MS Bingley and DW Davis Electron beam welding copperand dilute copper alloys BNF Report 608/7

Ten gradesof copper were examined, 3 PDO, 2 Tough pitch, 2 OFHC, 1 Copper Chromium alloy and 1 special high purity copper (as cast).
All except the last one was supplied as 75 mm wide x 15 mm thick bar stock. Eight were extruded and drawn whilst the ninth was hot and cold rolled.

Whilst some casting defects were apparent in the as cast materials, none were apparent after mechanical working.

All materials were analysed by BNF, some were checked by Pori-copper.

Oxygen and hydrogen levels were measured in as cast, as extruded and as welded bars. In the latter case checks were carried out on both the matrix surrounding the weld and the weld metal.

Electron Beam Processes of Chertsey England carried out the welding using 1. A 13.5 kW and 2. A 6 kW machine. The first was medium vacuum $5x10^{-2}$ Torr and the second was high vacuum $5x10^{-4}$. The second machine was only capable of partial penetration welds.

Pressure in the welding chamber was constantly monitored but the point is made that the pressure seen by the weld exceeds the pressure in the chamber owing to;

1. the pressure generated by the electron beam
2. the pressure due to vapourisation of the weld metal, and
3. the metallostatic head of the molten metal in the weld.

These factors may produce pressures in the weld of up to 0.05 atmospheres, (78 Torr) (TWI have used 80 kW and partial vacuum for lid welds, with higher vacuum and lower power for seam welds.)

The types of defects seen in association with welds were,

1. Superficial cracks, particularly in the weld root
2. Root porosity in partial penetration welds
3. Blowholes, and
4. Internal porosity.

The bottom surfaces of full penetration welds always contained pinholes and sometimes, minor cracks. Wells were formed on the back surface and it is acknowledged that this defect can be controlled using a backplate.

Usually gross porosity was obseved in the roots of partial penetration welds. The best results in this respect were obtained with the super-pure ingot ,closely followed by the OFHC. Results were much worse with PDO. Control of welding speed eliminated this defect in the OFHC material.
Blowholes form on the top surface, they have the width of the weld and in this work they frequently extended to the weld root. They occurred in every material examined in varying degrees and apparently at random.

At the high chamber pressure ($3x10^{-2}$ Torr) the effect was least for OFHC (3.4/m). In partial penetration welds made at lower pressure $5x\ 10^{-4}$ Torr, OFHC had the highest frequency of blowholes (109/m). Formation of blowholes was also sensitive to welding speed and power but chamber pressure was by far the dominant control parameter.
Weld quality was assessed. Radiography was only capable of clearly detecting major defects, mainly blowholes and root defects but there were some indications of porosity, few welds were defect free of weld root or blowholes and none were free of porosity.

Metallography confirmed the radiographic results. Pores were circular in cross section suggesting that they were due to gas evolution. In many cases the pores were in clouds, usually at the weld/matrix interface, but in the case of OFHC some were seen in the parent metal, larger pores were up to 0.3 mm in diameter.

All the defect types were found in all materials but the frequency of all types were lowest in super-pure and OFHC grades.

The Authors relate blowholes to instability in the electron beam, they comment that quality depends on run length and whilst short runs of weld (200 mm) may appear perfect longer runs may be impossible to achieve. Attempts to repair blowholes by rewelding failed. They also comment that material composition has an effect on the frequency of blowholes but they do not relate material composition to stability of the electron gun.

The authors refer to work by others on gas porosity and quote solubility products for various gasses at 1100^{o} C. They reiterate that the pressures seen by the weld may be in the range 8-40 Torr and suggest that average chamber pressure may be neglected when considering the gas reactions in the weld. Consideration of the solublity products and the measured concentration of gasses in the starting materials indicated that under the welding conditions used for the OFHC,- H_2S, SO_2, CO, H_2 and O_2 are unlikely to form. H_2O however was likely to form. They conclude that the most likely cause of porisity is the steam reaction. Best results were on OFHC with <2 ppm oxygen and <0.2 ppm hydrogen.

The analyses carried out by BNF and pori-copper differed somewhat in their results from samples of the same material. For OFHC material BNF quote a total impurity level of <64 ppm. Whilst poricopper quote <33 ppm. Some of this discrepancy may be accounted for by the difference in lower limits of detection claimed by the two groups, but this can not be the full story. BNF are lower on Sulphur than poricopper, 3 ppm compared with 7 ppm and higher on Tellurium 30 ppm compared with <3 ppm. This highlights the problems associated with analysing for such low levels of impurities. It is believed that at the time in question analytical standards were supplied to pori-copper by BNF.

8.8 T Stepinski Inspection of copper canisters for spent nuclear fuel by means of ultrasonic array system. SKB Project report 97-06 August 1997

The report describes the second phase of a programme to develop an automated ultrasonic inspection system for the lid welds on the copper-iron canister. It is particularly concerned with, evaluation of linear array transducers, development of software to model elastic fields in solids and an investigation of ultrasonic noise (backscattering) in copper.

The linear array transducer had 64 piezoelectric composite ceramic elements and overall dimensions 33.5 mm x 1mm. It was equipped for both fixed focus (ceramic delay lines) and variable focus (electronic delay lines). A focal length of 190 mm in water was used. The ultrasonic system was equipped to scan in three axes. A scans were digitally stored to enable construction of B scan or C scan images from a single data set. Step size on the scanner was 1mm.

Nine test blocks containing natural or artificial defects were examined using the array and or a single transducer. The linear array had a 3 MHz frequency and the single transducer had a centre frequency of 3.5 MHz and a diameter of 10 mm. The array was scanned electronically by selecting a beam aperture of sixteen array elements; this gives a very significant advantage in speed.

Four test blocks containing both natural and artificial defects were examined using the array. All artificial defects were reliably detected but porosity, which had previously been located radiographically, was not. The reason for this could have been the very non-ideal geometry of the specimens, which had large artificial plane reflectors that interfered with the ultrasonic signal but not the radiography.

The remaining five specimens were sections taken from an electron beam weld. They were examined using both the array and the single transducer systems. The array inspections were accomplished in a few minutes by using electronic scanning whist the single transducer inspection took several hours. The results from the two examinations were essentially similar, but the signal to noise ratios from the array were stronger owing to a reduced level of spatial averaging which arises from the differences in the sizes of the array and the single transducer. The defect resolution was also finer with the array for the same reason.

Whilst considerable further development of the array system is required before it is a practical tool, the indication is that it could have better defect detecting capability than the single focussed tranducer and that it will operate at much higher speeds.

The problem of grain boundary noise in copper is acknowledged and two methods for reducing grain noise are mentioned. The first is spatial averaging and the second, which is investigated, is split spectrum processing (SSP). The investigation made use of A scans from one of the test blocks and the processing was done electronically. The processing involves fast Fourier transformation (FFT) of the signals and elctronic filtering to remove grain noise.

The non-linear filter is a non-coherent detector (NCD) developed by the authors from radar and communications applications designed to detect transients embedded in background noise. It is implemented in Matlab® (from Mathworks) on a PC. At this stage the system is not fully automatic and it involves the operator in selecting a region containing only noise followed by testing on a standard defect to establish an estimated “noise co-variance matrix” to use in the further processing. The authors are encouraged by the results but they point out that the anisotropy of the crystals in a weld zone will add further complications that have so far not been addressed. They conclude that considerable further development is required before an operational system can be designed.

The purpose of the modelling of elastic fields in immersed solids is to understand and ultimately control the sound fields arising in an immersed solid from the interactions of both the longitudinal and transverse waves with the microstructure. This would enable deconvolution of detected signals and and defect detection and location. Review of the mathematical analysis presented is outside the scope of this review and of this writer.

The authors believe that they have developed modelling tools, which will enable them to make fast and efficient designs for beam forming schemes to use in inspection of copper. They also believe that they have demonstrated the feasibility of algorithms to reduce the effects of grain noise on degradation of signals. It is clear that considerable further work is required to prove their beliefs but if they are proved they will enable a significant advance in inspection technology which is highly relevant to the case of canister inspection.

8.9 H Jeskanen and P Kaupipinen, Ultrasonic inspection of electron beam welded joints in copper, Posiva working report 97-34e August 1997

Three test specimens were used. The first is a 50 mm thick hot rolled plate, 350 mm long, 310 mm wide and having an EB weld parallel to and 65 mm from one 350 mm edge. This specimen had side drilled holes parallel to the weld direction at depths of 12.5, 25 and 37.5 mm from the surface and on lines 5 mm to one side and 8 mm to the other side of the weld. The hole diameters are not given on the drawing. The second and third are calibration blocks cut from a simulated lid weld on flat plate. A full size lid weld on a tube section of depth 250 mm was also examined. The lid is forged and the tube is hot rolled material. No manufacturing details are given.

Specimen 1 was used as a test bed for selection of probes and measurement techniques.
Specimens 2 and 3 were cut from the simulated lid weld such that specimen 2 had a surface parallel to and 15 mm from the weld on the cylinder side and specimen 3 had a surface parallel to and 20 mm from the weld on the lid side. Both specimens were examined before and after a series of side drilled and flat-bottomed 3 mm diameter holes were drilled on each side of the weld.

Scanning with normal incidence probes was from the forged side of the specimen, that is perpendicular to the weld from the lid surface which gives a metal paths to the weld of 65 mm for specimen 2 and 20 mm for specimen 3. The frequency and dimensions of the probe are not given but it is said that the grain size of the weld and the forged material limits the frequency that can be used. It is said that defects close to the surface or breaking onto the surface are not detected by this method due to deflection of the beam, I think this a mistranslation and that he author means due to interference of the outgoing and incoming pulses. When both specimens were examined before drilling the artificial defects the noise from the weld was very high and no weld defects were detected. The weld root defect was detected and it was possible to use this to measure the depth of weld penetration.

A surface wave probe was used in attempts to observe near surface and surface breaking defects. This was used on the surface corresponding to the cylinder surface only, the reason for this is not clear but it could be because the grain size in the forged material is very coarse rendering the technique impractical. Before the artificial defects were drilled no indications were detected.

After the artificial defects were drilled the second specimen was examined from the forged side of the joint, that is with a metal path of 65 mm to the weld. All the side drilled holes were detected with signal levels well above the noise levels in the weld, these were 3 mm diameter and 25 mm long and it is reasonable to interpret that if they had been in the weld they would have been detected. Most of the flat bottomed holes, (3 mm diameter) were also said to be detected but the signal levels of all were below the noise level in the weld, it is stated that this indicates that if the defects were in the weld they would not have been detected. A calculation made by the authors suggests that the minimum defect size which could be detected in the weld is 3.3 to 4.8 mm diameter. This does not suggest that all defects of that size or larger would be detected if they were not ideally oriented with respect to the beam.

With a 70 ° angle probe having a focal depth of 10 mm the results for side drilled and flat bottomed holes were similar to the results using a normal incidence probe.

A 60° angled probe with a focal depth of 40 mm was also examined. Planar defects were not detected, cylindrical holes were detected, whilst no picture of the result is presented the quoted measurements indicate that the detection was reliable.

When the normal incidence probe was used to examine the full scale weld, the run in and run out defects which extended from the inner surface to the outer surface over a distance of 250 mm were detected. Defects arising from the beam leaving the intended weld line were also detected. The angle probes gave indications of large near surface craters that were not seen using the normal incidence probe.

The authors conclude that with carefull choice of probe and inspection procedure defects which are larger in diameter than 5 mm and favourably oriented with respect to the beam may be detected. This does not mean that defects larger in diameter than 5 mm will not be missed.
If STUK consider that this inspection will be satisfactory they must have set a very relaxed quality standard.

8.10 P Auerkari and S Holmstrom Long term strength of EB welds of the canister for nuclear disposal, Posiva working report 97-35e September 1997

Tests are reported on creep specimens taken to include lid welds at their centre line. The material used was said to be OF copper plate of grain size 150 µm and sulphur content 5 ppm, it also contained 40 ppm phosphorus.

All failures occurred in the centre of the welds along grain boundaries and this is given as evidence that the welds are weaker in creep than the bulk material. This is likely to be the case since phosphorus added to increase the creep strength of the bulk material should have been zone refined out of the weld. Results from eleven specimens are reported, although twenty seven were made, the reported tests covered the temperature range 20 to 200° C and lives from 4 minutes to 7000 hours.

All specimens were strained into the plastic region during loading for the test and in seven cases this was by more than 10%. This is a very unusual strain level to start a creep test and not at all representative of the real case.
Minimum strain rates have been measured as a function of applied stress at four temperatures, for each temperature, 20, 100, 150 and 200 °C. these have been used to construct minimum strain rate over stress plots, the strain rate axis is logarithmic and it extends over six decades. The stress axis is also logarithmic and it extends from 60 to 180 MPa. Not surprisingly the data have been fitted to straight lines even though three of the lines have only three points and the fourth has only one point. The

minimum strain rate value has been used to estimate lives of specimens which did not fail and the whole batch of results have been included on a Larson Miller plot with the published results of Henderson.

Three of the results, one of which is estimated and all of which are the three longest duration tests lie on a line which is parallel to the line produced by Henderson, the remaining points lie on a line of higher slope (all slopes are negative). This is interpreted as a change in mechanism when the creep stress is below a critical value. The Larson Miller plot for the low stress data, three points, (one estimated) was used to estimate safe lives for the real case by using the linear life fraction rule for lives out to 100000 years. The author concludes that the safe stress for 100,000 years is in excess of 110 MPa, since the likely stress is claimed to be less than 75 MPa a considerable margin of safety exists.

Whilst the author has demonstrated considerable ingenuity in extracting information from a less than minimum requirement of data, this reviewer feels that the degree of extrapolation exercised together with the level of uncertainty in the data and its interpretation renders the conclusions reached unsafe.