

Från: Peter Szakalos szakalos@kth.se  
Ämne: FW:  
Datum: 3 juni 2009 12:55  
Till: johan.swahn@mkg.se

---

Hej Johan!

CC:ar den korrespondens jag har med Stephan.

mvh Peter

Peter Szakálos  
KTH, division of Surface- and Corrosion Science, DKV 51, SE-10044 Stockholm  
[www.corrosionscience.se](http://www.corrosionscience.se)  
and  
Szakálos Materials Science AB  
Fridhemsgatan 29b, SE-11240 Stockholm  
Mobile: +46707537946

---

From: Kaufhold, Stephan [Stephan.Kaufhold@bgr.de]  
Sent: 03 June 2009 09:50  
To: Peter Szakalos  
Subject: AW:

Dear Peter,

Many thanks for the detailed answer.

Unfortunately we do not have any experience with copper and bentonite. We are working together with the Max Planck Institute for iron research in Düsseldorf since two years now and we managed to identify the most probable corrosion mechanism (which we will publish now). In fact a part of this project was also to investigate the bentonite copper interface but we have not done much about it. The key of our research is to use 40 different but very well characterized bentonites which can lead to some kind of understanding of the different corrosion mechanisms. In case of copper we learned from the LOT experiment that S is supposed to play a role. This does not mean that corrosion does not occur in case of S-absence but surely different corrosion products will be obtained. We hope to get the financial support for going on with this fruitful collaboration.

Best regards,  
Stephan

-----  
Dr. Stephan Kaufhold  
<http://www.bgr.bund.de/kaufhold>  
-----

-----Ursprüngliche Nachricht-----

Von: Peter Szakalos [mailto:szakalos@kth.se]  
Gesendet: Tuesday, June 02, 2009 11:54 PM  
An: Kaufhold, Stephan  
Betreff: RE:

Dear Stephan,

1) OK!

2) OK, because I used only your quantitative data (XRF, Table 2) and got a somewhat higher value of around 3.7  $\mu\text{m}/\text{y}$  in corrosion rate which should be multiplied by a "constant" which is around 3 (not 5 as I guessed earlier). Anyway, it ends up with a total corrosion rate in the order of 10  $\mu\text{m}/\text{y}$  which is around 5000 times higher than the corrosion rate SKB AB calculate with in the "Safety analysis". The temperature in the repository will of course not be as high as for your

examined block 15 for a long time but anyway...

3) Hmm, difficult question. Swedish groundwater contains chlorides (high amount) and sulphides and is really aggressive. It is known that ordinary stainless steels do corrode by localized attack during long time exposures. There are some experience with high alloyed stainless steels, nickel base alloys and titanium alloys exposed, let us say for around 10 years, but what about hundreds or thousands of years? By adding a "mantle" of a corrosion resistant alloy on the "naked" copper canister it is possible to protect it from rapid corrosion during the initially hot period. Eventually, IF the outer mantle start to corrode, it will act as a sacrificial anode for a long time since copper is a more noble metal. By that time the canister should be as cold as the surrounding groundwater, i.e around 15 degrees Celsius and the copper corrosion rate should be at a sub-micron rate per year at that temperature. The problem with with the use of only one layer of corrosion resistant material (or "steel") is that there is no guarantee for an eventual initiation of localized corrosion after hundreds or thousands of years. A bi-metal canister with a corrosion resistant and "sacrificial" outer shell would be safer.

By the way, do you have any experience with Cu/bentonite exposures at lower temperatures?

Best Regards /Peter

Peter Szakálos  
KTH, division of Surface- and Corrosion Science, DKV 51, SE-10044 Stockholm  
[www.corrosionscience.se](http://www.corrosionscience.se)  
and  
Szakálos Materials Science AB  
Fridhemsgatan 29b, SE-11240 Stockholm  
Mobile: +46707537946

---

From: Kaufhold, Stephan [Stephan.Kaufhold@bgr.de]  
Sent: 02 June 2009 11:25  
To: Peter Szakalos  
Subject: AW:

Dear Peter,

1) yes,  $\mu$ -EDXRF is only qualitative and the profile was adjusted according to the XRF data. As I told you, we'll have better data next time, where we'll try to sue microprobe analysis, or at least ESEM-EDX.

2) you mean the error bar? This is actually not the error but the area which was sampled. We took the block and drilled a hole with a borer which had a diameter of appr. 1 cm. We gained 5 g and 1.5 g was analyzed by XRF. Using more than 1 g for XRF provides a perfect accuracy. Actually our XRF section operates two XRF spectrometer in parallel in order to resolve possible coincidences. I'd not claim that this analysis is perfect but our XRF team is actually doing the best which is possible, I suppose. They use more than 700 standards for annual calibration and take part in several international round robins. In conclusion: I trust the data but the actual sampling position provides the error.

3) I'm just curious: Do you think that "protected copper" is better than steel?

Best regards,  
Stephan

-----  
Dr. Stephan Kaufhold  
<http://www.bgr.bund.de/kaufhold>  
-----

-----Ursprüngliche Nachricht-----

Von: Peter Szakalos [mailto:[szakalos@kth.se](mailto:szakalos@kth.se)]  
Gesendet: Freitag, 5. Juni 2009 11:04 AM

Gesendet: Tuesday, June 02, 2009 11:04 AM  
An: Kaufhold, Stephan  
Cc: johan.swahn@mkg.se  
Betreff: FW:

Dear Dr Kaufhold,

I have some question about the Cu-profiles. As I understand, it is only the XRF results (page 9, Table 2) that is quantitative, the my-EDXRF profiles is only qualitative (relative intensity)? The XRF results in Figure 6 have a large radial scatter, 10 mm, does it mean that clay from a 10 mm area is analysed? How much clay is used per analysis?

Best Regards/ Peter

Peter Szakálos  
KTH, division of Surface- and Corrosion Science, DKV 51, SE-10044 Stockholm  
[www.corrosionscience.se](http://www.corrosionscience.se)  
and  
Szakálos Materials Science AB  
Fridhemsgatan 29b, SE-11240 Stockholm  
Mobile: +46707537946

---

From: Peter Szakalos  
Sent: 28 May 2009 19:32  
To: Kaufhold, Stephan; johan.swahn@mkg.se  
Subject: RE:

Yes, 10 or even 2  $\mu\text{m}$  is too much and we, researchers at KTH, believe that the "naked" copper canister must be protected with a corrosion resistant metal to withstand the "initially" hot period (at least 1000 years). However, it seems to take some more time for us to convince the company SKB AB that copper corrosion is a serious problem...  
Anyway, if I understand you correctly, the copper tube (or any part of it) was never sent to BGR, only the bentonite?

Best Regards/ Peter

Peter Szakálos  
KTH, division of Surface- and Corrosion Science, DKV 51, SE-10044 Stockholm  
[www.corrosionscience.se](http://www.corrosionscience.se)  
and  
Szakálos Materials Science AB  
Fridhemsgatan 29b, SE-11240 Stockholm  
Mobile: +46707537946

---

From: Kaufhold, Stephan [Stephan.Kaufhold@bgr.de]  
Sent: 28 May 2009 15:25  
To: Peter Szakalos; Johan Swahn  
Subject: AW:

Hello back,  
Sounds very reasonable, of course my calculations were only based on the Cu in the bentonite. If Cu was actually transported away from the tube then it will be impossible to calculate a corrosion rate. Concerning your question: No, I haven't seen the Cu tube or anything. I just received a sample block but as given in my report, one could observe the covelline like phases at the very contact. Hence I would expect that there is more corroded Cu at the very contact which - of course - is not included in my calculation.  
By the way, 10  $\mu\text{m}$  is rather a lot, isn't it ? Wouldn't it be better to use steel ?  
Best regards

Best Regards,  
Stephan

-----  
Dr. Stephan Kaufhold  
<http://www.bgr.bund.de/kaufhold>  
-----

-----Ursprüngliche Nachricht-----

Von: Peter Szakalos [mailto:szakalos@kth.se]  
Gesendet: Thursday, May 28, 2009 3:16 PM  
An: Johan Swahn; Kaufhold, Stephan  
Betreff: RE:

Hello!

I think Dr. Kaufhold's calculation is correct based on the amount of copper in the bentonite, but it should be a really conservative value since copper ion "solubility" at higher temperature is significant in the water close to the canister (and pore water in the bentonite). Additionally, a part of the corrosion product should be attached to the copper surface, i.e a layer with 100% copper corrosion products?

My estimation was based on copper profile data from copper/bentonite exposures in Canada (F. King et al.) where he correlated the profiles with actual weight loss measurement. Roughly, if I remember correct, by multiplying the corrosion rate based on "Cu- profile in bentonite" with around 5 it gave the "true" total corrosion rate. In your case around 10 micrometer per year. Of course this "constant" could be somewhat different in Äspö, larger or smaller, but definitely larger than one.

Dr Kaufhold, have you seen the copper tube surface, what was the visual appearance?

Best Regards Peter

Peter Szakálos  
KTH, division of Surface- and Corrosion Science, DKV 51, SE-10044 Stockholm  
[www.corrosionscience.se](http://www.corrosionscience.se)  
and  
Szakálos Materials Science AB  
Fridhemsgatan 29b, SE-11240 Stockholm  
Mobile: +46707537946

----- Forwarded Message

From: "Kaufhold, Stephan" <Stephan.Kaufhold@bgr.de>  
Date: Thu, 28 May 2009 13:34:19 +0200  
To: Johan Swahn <johan.swahn@mkg.se>  
Subject: AW: AW: Appendix 6 of the LOT A2 draft report

Yes, the accuracy of my calculation strongly depends on the accuracy of the Cu content of the first mm. The XRF scanner provided a nice profile but unfortunately no absolute figures. Hence the profiles were adjusted according to the XRF values. Actually if you compare the calculation 1 and 2 you will see that there is a significant difference. In case of calculation 2 the Cu profile was simply assumed to be linear and let go through the 1 cm XRF value which is considered to be rather accurate. If you look at profile 1 you can see that it does not go through this value. If one believes in the 1 cm value then a corrosion rate of  $4 \mu\text{m/a/cm}^2$  was calculated. What are the corrosion rates calculated by the other labs?

-----

Dr. Stephan Kaufhold  
<http://www.bgr.bund.de/kaufhold>  
-----

-----Ursprüngliche Nachricht-----

Von: Johan Swahn [mailto:johan.swahn@mkg.se]  
Gesendet: Thursday, May 28, 2009 1:15 PM  
An: Kaufhold, Stephan  
Betreff: Re: AW: Appendix 6 of the LOT A2 draft report

Stephan,

I have understood that there is an uncertainty as to what the corrosion rate has actually been. The corrosion rate depends on the temperature and how saturated the clay has been. The rate you calculated is lower than the rate calculated by a Peter Szakalos at the Royal Institute of Technology in Stockholm using the figures in your table 2. I will forward your e-mail to him so that he could contact you to compare with you.

Best regards,

Johan

On 2009-05-28 11.04, "Kaufhold, Stephan" <Stephan.Kaufhold@bgr.de> wrote:

Yes, you are right - brilliant idea.  
I directly started to calculate !!  
I established the possibility to adjust the Cu profile manually instead of using a mathematical function (because it is more flexible).  
I tested two Cu profiles, the first based on the XRF-scanner data and the second one based on the XRF data.  
But here, of course, is a great source of error because I termed the first sample 1st mm but of course I was not able to scratch off the sample from the block with an accuracy of 0.01 mm. We just took a knife and scratched off approximately the first mm (accuracy 0.5 mm). Therefore I like the XRF scanner data because there was no sampling necessary. Next time we will try to profile the block with the microprobe (in case we are able to prepare the sample properly).  
Anyway, I'd suppose that the corrosion rate is around 2 µm/year. Does this fit with other calculations?  
I attached the file which I used for calculation so you can play with the blue figures (=variables) and of course check if I calculated correctly.  
Best regards,  
Stephan

-----  
Dr. Stephan Kaufhold  
<http://www.bgr.bund.de/kaufhold>  
-----

-----Ursprüngliche Nachricht-----

Von: Johan Swahn [mailto:johan.swahn@mkg.se]  
Gesendet: Thursday, May 28, 2009 8:04 AM  
An: Kaufhold, Stephan  
Betreff: Appendix 6 of the LOT A2 draft report

Dear Dr. Kaufhold,

I have from the Swedish Nuclear Fuel and Waste Management Company SKB received the draft report with the results from the LOT A2 package at the Äspö Hard Rock Laboratory with appendices. Appendix 6 to thye report is your report on the mineralogical and geochemical alteration of the MX80 bentonite from the experiment. I enclose it.

I have been considering an issue that I wonder whether you could possibly ssist me with. From the data in table 2 on the copper content in the clay, would it be possible to estimate, even very roughly, the amount of copper that has corroded from the copper pipe per square cm. Knowing the time of heating was approximately 5 years perhaps a mean corrosion rate in micrometers per year could then be estimated, even if it was a rough figure.

Best regards,

Dr. Johan Swahn

----- End of Forwarded Message