Release kinetics of electrochemically deposited antibacterial copper from anodized titanium implant surfaces

A Kessler[1], L Straumann[1], U Pieles[1], M de Wild[1], C Jung[2],
[1] *University of Applied Sciences Northwestern Switzerland, School of Life Sciences, Muttenz, CH*
[2] *KKS Ultraschall AG, Medical Surface Center, Steinen, CH*

INTRODUCTION: Functionalizing implant surfaces by antibacterial agents reveals as a promising strategy to reduce infection risk appearing immediately or years after medical implant placement. We have recently established an electrochemical method to deposit antimicrobial copper on anodized titanium samples [1, 2]. First studies indicated that only ~25% of Cu are released into simulated body fluid (SBF) after release time of one year (studies at 37°C and 80°C) [1]. Here we report the release kinetics in more detail. It is observed that calcium present in SBF facilitates apatite formation at the implant surface which reduces copper release.

METHODS: Discs of cpTi were anodized according to the spark-assisted anodizing method [1, 2]. Copper was electrochemically deposited using proprietary electrolyte and process parameters (KKS TioCel^{TM}). The amount of deposited Cu per disc was determined by dissolving Cu in 65% nitric acid at 50°C over night. Cu concentration was determined by atom absorption spectroscopy (AAS, Perkin Elmer, AAnalyst 800, graphite furnace, 324.8 nm) as well as inductively-coupled-plasma mass spectrometry (ICP-MS, Agilent 7500cx). Release studies were performed at 37°C for 14 days followed by an accelerated aging during another 14 days at 80°C (Arrhenius accelerated release, total simulated extraction duration: 289.8 days). Aliquots of SBF (SIGMA, Earl's balanced salt solutions E6267 and E3024) were taken from the incubation vessel after certain time intervals and the amount of Cu was quantified by AAS and ICP-MS.

RESULTS: After 289.8 days in SBF E6267 (no Ca), the cumulated release of Cu from the Ti surface corresponds to the total Cu amount per disc. The release rate decreases with extraction time (Fig. 1). Accordingly, Cu was no more detected on the discs by SEM/EDX after the end of the release experiment (Fig. 2 bottom). Studies with SBF containing calcium (E3024) indicated a qualitatively similar course of the release curve, however with a more pronounced decrease of the rate and lower Cu contents. Interestingly, here SEM after the release experiments revealed dense apatite formation (molar ratio Ca/P: 1.57), see Fig. 2 top. Cu was still detectable on the surface by EDX. In addition, Cu adsorbed at the surface of the glass vials was observed, however, only in the presence of Ca.

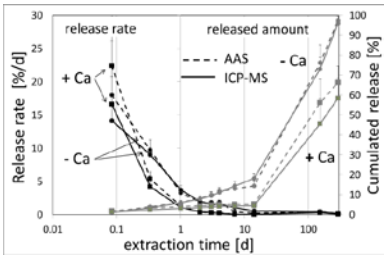

Fig. 1: Mean release rate for Cu (n = 4, SBF E6267) and cumulated Cu amount logarithmically plotted against the extraction time.

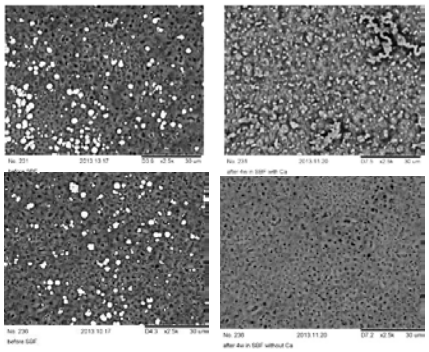

Fig. 2: SEM pictures of copper deposited discs before (left) and after (right) the release experiment in E3024 (top) and E6267 (bottom).

DISCUSSION & CONCLUSIONS: The Cu release rate as function of the extraction time follows known release profiles independently of the presence of calcium. The amount of detectable released Cu is significantly lower in the presence of Ca because (i) apatite growth on the discs hinders Cu leaching and (ii) part of Cu together with Ca is adsorbed at the vial glass.

REFERENCES: [1]C. Jung, N. Ryter, J. Köser, W. Hoffmann, L. Straumann, N. Balimann, F. Meier, M. de Wild, F. Schlottig, I. Martin, U. Pieles (2012) *eCM*, **23** (Suppl 1):16. [2]C. Jung (2010) *eCM*, **19** (Suppl 2):4.

ACKNOWLEDGEMENT: CTI funding (N° 14293 2 PFNM-NM) is acknowledged.