



Contents lists available at ScienceDirect

## Regulatory Toxicology and Pharmacology

journal homepage: [www.elsevier.com/locate/yrtph](http://www.elsevier.com/locate/yrtph)

# Bioaccessibility of micron-sized powder particles of molybdenum metal, iron metal, molybdenum oxides and ferromolybdenum – Importance of surface oxides



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## ARTICLE INFO

## Article history:

Received 2 March 2015

Available online 29 May 2015

## Keywords:

Molybdenum  
Ferromolybdenum  
Alloy  
Bioaccessibility  
Surface oxide

## ABSTRACT

The European chemical framework REACH requires that hazards and risks posed by chemicals, including alloys and metals, that are manufactured, imported or used in different products (substances or articles) are identified and proven safe for humans and the environment. Metals and alloys need hence to be investigated on their extent of released metals (bioaccessibility) in biologically relevant environments. Read-across from available studies may be used for similar materials. This study investigates the release of molybdenum and iron from powder particles of molybdenum metal (Mo), a ferromolybdenum alloy (FeMo), an iron metal powder (Fe), MoO<sub>2</sub>, and MoO<sub>3</sub> in different synthetic body fluids of pH ranging from 1.5 to 7.4 and of different composition. Spectroscopic tools and cyclic voltammetry have been employed to characterize surface oxides, microscopy, light scattering and nitrogen absorption for particle characterization, and atomic absorption spectroscopy to quantify released amounts of metals. The release of molybdenum from the Mo powder generally increased with pH and was influenced by the fluid composition. The mixed iron and molybdenum surface oxide of the FeMo powder acted as a barrier both at acidic and weakly alkaline conditions. These findings underline the importance of the surface oxide characteristics for the bioaccessibility of metal alloys.

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## 1. Introduction

REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) is a European Chemicals Directive first implemented in July 2007. Its aim is to evaluate, document and restrict the application and progression of chemicals manufactured and processed in the European Union in quantities that exceed 1 tonne per company and year (EC, 2007). Within REACH, metals are considered as substances for which registration dossiers have to be submitted. Such dossiers include the assessment of the toxicological and ecotoxicological hazard profile, for which the specific bioaccessibility in biological fluids plays an important role. Bioaccessibility is here defined as the pool of released metals from a metal or alloy that potentially can become available for absorption by an organism and is measured as the total amount of released metal species in solution after separation from the powder particles. The bioavailable fraction of released metal species in solution may be

significantly lower compared with the total concentration. However, this was not studied within the scope of this paper.

Alloys are generally considered as special mixtures under REACH, for which no registration dossiers need to be prepared. So far, very few alloys on the market have been investigated individually. An alloy is as “a metallic material, homogeneous on a macroscopic scale, consisting of two or more elements so combined that they cannot be readily separated by mechanical means” (EC, 2009). An alloy is hence totally different from a chemical mixture. One or several elements are intentionally added to the base element, which constitutes the largest percentage of the material, to gain specific mechanical or physico-chemical properties compared with its pure alloy components. These changes in intrinsic properties make any translation, such as metal release rates of individual elements to an alloy of the same elements inaccurate and irrelevant. As a result, properties of alloys are in need of evaluation based on its alloy specific characteristics, and not on its pure constituent metals. Potential health risks of alloys have in some cases been estimated via read-across from the properties of the respective pure metals. However recent studies show that the surface properties of alloys are more important than their bulk

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composition, and that read-across from pure metals is often highly erroneous (Hedberg et al., 2013; Herting et al., 2005; Hillwalker and Anderson, 2014; Stockmann-Juvala et al., 2013).

Metal release from metals and alloys, without contribution of wear, is mainly governed by oxidation of the metal (corrosion) and of chemical dissolution of the surface oxide. These processes depend on the passive properties of the surface oxide (hinders corrosion) and, among others, the pH and metal complexation capacity of the surrounding fluid (Hedberg et al., 2011b; Hedberg and Midander, 2014; Mazinanian et al., 2015). Available corrosion and metal release studies in the literature on molybdenum-containing alloys are mainly focused on alloys (and metals) commonly used in technical or medical applications (e.g. corrosion-resistant stainless steel or implants) (Cobb and Schmalzreid, 2006; Hanawa, 2004; Hedberg and Odnevall Wallinder, 2014; Hedberg et al., 2014; Hillwalker and Anderson, 2014; Ichinose et al., 2003; Karimi et al., 2012; Lewis et al., 2005; Metikoš-Huković et al., 2006; Okazaki and Gotoh, 2005, 2008; Öztürk et al., 2006; Wataha, 2000). However, metal release data from molybdenum-containing biomedical implants may not necessarily follow similar trends as observed for pure molybdenum metal or ferromolybdenum alloys, as the corrosion properties of these materials are largely different (Hodgson et al., 2004; Kocijan et al., 2004). Mechanistic metal release investigations of molybdenum metal, ferromolybdenum alloys, or molybdenum oxides are scarcely reported in the scientific literature, despite their increasing use in different applications during the last decades. Molybdenum or molybdenum oxide nanoparticles are for example used for bio-diagnostics and energy storage applications as well as in polymers (Chan et al., 2005; Lee et al., 2009; Sengupta et al., 2014). Molybdenum shows relatively low acute toxicity, when taken up via the oral, dermal or inhalation route (OECD CoCAM programme, 2013).

The aim of this study is to correlate particle characteristics and surface composition with the extent of metal release from micron-sized powder particles of molybdenum (Mo) metal, iron (Fe) metal, and a ferromolybdenum (FeMo) alloy into five synthetic body fluids of relevance for the human exposure routes of dermal contact, inhalation and ingestion. Parallel comparative studies were performed on MoO<sub>2</sub> and MoO<sub>3</sub> powder particles.

## 2. Materials and methods

### 2.1. Investigated particles

This investigation includes the following micron-sized powder particles; (i) molybdenum (Mo) metal (>99.95 wt%), CAS No. 7439-98-7, Batch No. C198, produced by CM CHEMIEMETALL GmbH, Bitterfeld, Germany, (ii) a ferromolybdenum (FeMo) alloy (Mo content 69.8 wt%), CAS No. 94277-04-0, Batch No. 1010/07/2, produced by Treibacher Industrie AG, Treibach-Althofen, Germany, (iii) iron metal (Fe, >99.8 wt%), CAS No. 7439-89-6, Batch No. 1946672, produced by Höganäs AB, Höganäs, Sweden, (iv) molybdenum(IV)oxide (MoO<sub>2</sub>, >99.99 wt%), CAS No. 18868-43-4, Batch No. D1308 DRO, produced by CM CHEMIEMETALL GmbH, Bitterfeld, Germany, and (v) molybdenum(VI)oxide (MoO<sub>3</sub>, >99.99 wt%), CAS No. 1313-27-5, Batch No. RTPOC0080G, produced by Climax Molybdenum Company, Rozenburg/Rotterdam, Netherlands.

### 2.2. Cyclic voltammetry using a graphite paste electrode

Each molybdenum-containing powder (Mo, FeMo, MoO<sub>2</sub>, MoO<sub>3</sub>) was mixed with graphite powder (natural, briquetting grade, 100 mesh, 99.9995% (metal basis), UCP-1 grade, Ultra "F" grade, Lot

No. 61200620, Alfa Aesar, Sweden) in a ratio of 100 mg graphite and 1, 5, or 10 mg metal/alloy/oxide powder. This mixture was gently pressed and mixed with a pestle. A few drops of the electrolyte [8 M NaOH (pH 13.6), a solution of sodium acetate/acetic acid (0.1 M sodium acetate, 0.1 M acetic acid, pH 4.62), or 1 M HCl (pH 0)] were added to obtain a paste. The paste was positioned into a small ( $\varnothing$  1.9 cm, height 7.0 cm) glass container connected with a platinum wire to act as the working electrode. The counter electrode (a platinum wire wrapped around the reference electrode) and the reference electrode (Ag/AgCl sat. KCl) were positioned approximately 1 cm from the graphite paste in the electrolyte. The system was, prior to the measurements, allowed to equilibrate before determining the open circuit potential (OCP) for 300 s (or until the change of OCP was less than 1  $\mu$ V/s). The potential was then swept cathodically (to more negative potentials) starting at the OCP at a rate of 0.0005 V/s toward a potential of approximately -1.4 V (vs. Ag/AgCl sat. KCl), after which the potential was swept anodically until a potential of approximately +0.2 V.

### 2.3. Raman spectroscopy

Raman spectroscopy measurements were conducted using a Horiba HR800 Raman (Yvon Jobin) instrument using a 785 nm laser and an Olympus 50X objective. The laser power was attenuated to avoid sample damage. A visual inspection (optical microscope) was made prior to, and after each measurement, to ensure minimized sample destruction (via oxidation by the laser). In the case of visible sample destruction, the spectrum was not taken into account. Presented results are based on average spectra accumulated for 35 s at 3–5 different sample locations (MoO<sub>2</sub>, FeMo), or one sample location (Mo, MoO<sub>3</sub> – no signal for Mo, very strong signal for MoO<sub>3</sub>). No sufficient signal was obtained for the Fe powder, even with a 514 nm laser, a 100X objective, and an accumulation time of 60 s, and without any laser attenuation.

### 2.4. X-ray photoelectron spectroscopy

With X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS UltraDLD X-ray photoelectron spectrometer (Kratos Analytical, Manchester, UK) driven by a monochromatic 150 W Al X-ray source, the outermost (approx. 5 nm) surface of the powder particles was investigated. The analyzed areas were approximately sized 700  $\times$  300  $\mu$ m. Wide spectra measurements were performed to probe elements in the top surface of the powder particles. With a pass energy of 20 eV, detailed spectra for the main compositional elements of each powder, carbon (C 1s), oxygen (O 1s), nitrogen (N 1s), iron (Fe 2p) and molybdenum (Mo 3d) were obtained. The powders were mounted on copper tape to fix them against diffusion in the applied vacuum inside the ultra-high vacuum instrumental chamber. All binding energies were corrected to the carbon C 1s contamination peak at 285.0 eV. All peak areas were determined by assigning a linear base line. For the calculation of atomic ratios of oxidized metal and oxygen, the metal peak (only detected for Mo at 228.4  $\pm$  0.4 eV) was subtracted. Oxygen connected to any oxidized carbon compounds from the ambient air was not subtracted, however, its contribution was considered small due to the lack of (Mo-metal powder) or minor presence of oxidized carbon peaks (FeMo alloy, MoO<sub>2</sub>, and MoO<sub>3</sub> powders).

### 2.5. Measurement of specific surface area by nitrogen adsorption

The surface area to weight ratio (specific surface area) of each powder was estimated using the Brunauer–Emmet–Teller method (Brunauer et al., 1938) (Micromeritics GEMINI V) that measures the adsorbed amount of nitrogen at cryogenic conditions. The

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