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HYDROTHERMALLY SHORT TITLE: AQUEOUS HG
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TITLE: REAL-TIME MONITORING OF AQUEOUS Hg^{2+} REDUCTION DYNAMICS BY MAGNETITE / IRON METAL COMPOSITE POWDERS SYNTHESIZED HYDROTHERMALLY

SHORT TITLE: AQUEOUS Hg^{2+} REDUCTION DYNAMICS BY MAGNETITE / ZVI POWDER

Fabrice Brunet^{1,*}, Delphine Tisserand¹, Martine Lanson¹, Benjamin Malvoisin¹, Mathieu Bertrand²
& Céline Bonnaud²

¹ ISTERRE, Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, IRD, Univ. Gustave Eiffel, 38000 Grenoble, France

² HYMAG'IN, 38000 Grenoble, France

* Corresponding author

ABSTRACT

An iron-based powder material composed of zerovalent iron (8 wt.%) and magnetite (92 wt.%), has been synthesized hydrothermally at 200 °C from zero-valent iron. Its effect on the reduction of aqueous Hg^{2+} into gaseous Hg^0 has been investigated at ambient conditions for pH comprised between 4 and 8.5. The production of Hg^0 was monitored with an online mercury vapor analyzer at the picogram level for concentrations of iron-based composite of a few tenths of mg L^{-1} . Starting from a solution containing Hg^{2+} concentration of 25 ng L^{-1} at pH = 4, a succession of two Hg^0 production events was recorded. The first event is related to the Hg^{2+} reduction by ZVI which fully dissolved within the first hours. Upon ZVI consumption, pH drifted towards the pH window where magnetite can efficiently reduce Hg^{2+} at the hour timescale, resulting in a second Hg^0 production peak. The combined use of ZVI and magnetite to remove aqueous Hg^{2+} by formation of Hg^0 (volatile) under mild acidic pH allows (1) to maximize the Hg^{2+} reduction rate and (2) to take benefit of the longer lifetime of magnetite compared to ZVI.

KEYWORDS: ZVI; Hg removal; CV-AAS; Hg reduction kinetics; Steel-industry wastes

HIGHLIGHTS

- New experimental set-up for the in-situ monitoring of Hg⁰ resulting from the reduction of aqueous Hg²⁺ by iron oxide suspensions.
- Hg⁰ production bursts from a highly diluted HgCl₂ solution (25 ng L⁻¹) reacting with magnetite – zerovalent iron (ZVI) composite powder are monitored on a time-resolved basis.
- The respective contributions of magnetite and ZVI to Hg²⁺ reduction are deciphered.
- Magnetite and ZVI are not efficient to reduce Hg²⁺ in the same pH window.
- The advantages of mixing ZVI and magnetite to remove aqueous Hg²⁺ under acidic to slightly acidic conditions are shown.
- The magnetite – ZVI composite powder is obtained from commercial ZVI submitted to a hydrothermal treatment that can be applied to iron metal from the steel wastes.

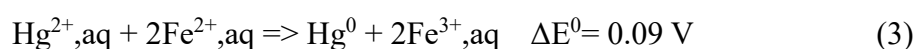
INTRODUCTION

Simple iron-based compounds such as iron metal, iron oxides and hydroxides show a great potential for the removal of pollutants by various physico-chemical processes such as adsorptive removal or photocatalytic degradation (*e.g.*, Mueller *et al.* 2012; Gusain *et al.* 2019; Gil-Diaz *et al.* 2021; Geneti *et al.* 2022). Fe²⁺ and Fe⁰ can also act as electron donors to convert the contaminant into a less soluble (Ponder *et al.* 2000; Crane *et al.* 2015) or a less toxic form (Zhang 2003; Liu & Wang 2019).

Actually, the steel industry produces hundreds of million tons of Fe-rich wastes yearly (Brunet 2019) that can be processed hydrothermally to obtain Fe₃O₄ nanoparticles (Crouzet *et al.* 2017). They can be valorized for the remediation of contaminated soils and groundwater. Here, the hydrothermal process proposed by Crouzet *et al.* (2017) to recycle ferrous wastes into nanomagnetite has been applied to a commercial powder of zerovalent iron (ZVI). The process was stopped before complete conversion of ZVI into magnetite, so that about 8 wt.% of ZVI remained unreacted. The recovered composite magnetite – ZVI product, called M/ZVI herein, was investigated for its capacity to reduce aqueous Hg²⁺ over a range of pH comprised between 2 and 8.5. Indeed, Hg has been recognized as an element of global concern (UN Environment 2019). Mercury (Hg) bioaccumulates in the form of methylmercury which is highly neurotoxic to both human and aquatic systems (*e.g.*, Clarkson and Magos 2006). Indeed, monomethylmercury, (CH₃Hg⁺), is formed from Hg²⁺ species under the activity of bacteria in anoxic media, the best known being iron- and sulfate-reducing bacteria as well as methanogens (Hellal *et al.* 2015, Gilmour *et al.* 2013, Gilmour *et al.* 2018). Established or emerging methods for Hg remediation do already exist using physical, chemical or

biological routes (Guneý *et al.* 2020). Among them, nano-FeS and γ -Fe₂O₃ (Ramezani *et al.* 2016) can be used to immobilize Hg but an additional step is necessary to convert Hg²⁺ into Hg⁰.

Both ZVI and magnetite have the potential to reduce aqueous Hg²⁺ according to three basic redox reactions (standard redox potentials are from White & Peterson 1996 and Bard *et al.* 1985):



White and Peterson (1996) showed that the half-cell potential for solid-state oxidation of ferrous iron in magnetite, noted $[\text{Fe}^{2+}]_{\text{Fe}_3\text{O}_4}$ in R.2, into ferric iron in maghemite, noted $[\text{Fe}^{3+}]_{\text{Fe}_2\text{O}_3}$ in R.2, falls in the -0.35 V to -0.65 V range. This means that magnetite (R.2) is a stronger reducing agent than aqueous Fe²⁺ (R.3). Homogeneous reduction of Hg²⁺ by aqueous Fe²⁺ according to R.3 has been reported experimentally (Amirbahman *et al.* 2013) and was shown to be catalyzed by the presence of hematite and goethite surfaces.

The reduction kinetics of aqueous Hg²⁺ into Hg⁰ according to R.2 has been studied by Wiatrowski *et al.* (2009) and was found to follow a pseudo first-order rate law. The kinetics is favored by increasing pH in the 4.8 – 6.7 range, increasing magnetite surface area and decreasing chloride concentration. For a Fe₃O₄ surface area of 2 m² L⁻¹, over 80% of the measured Hg²⁺ loss (100 nM HgCl₂) occurred in less than 15 min. Electron transfer between iron and mercury is believed to proceed through a Hg²⁺ adsorption step onto the magnetite surface.

The removal rate of aqueous Hg²⁺ by nanoparticles of zerovalent iron (nZVI) supported on pumice, *i.e.*, according to R.1, has been investigated by Liu *et al.* (2014) in the 3.11 – 8.13 pH range. With a nZVI surface area of 32.2 m² g⁻¹ (BET), above 98% of Hg²⁺_{aq} (60 mg L⁻¹) removal was achieved within minutes. High-resolution XPS showed a short Hg²⁺ adsorption step (< 30 sec) onto nZVI surface before it was reduced into Hg⁰. Using nZVI (30 m² g⁻¹, 2 g L⁻¹), Yan *et al.* (2010) obtained 98% of aqueous Hg²⁺ (40 mg L⁻¹) removal in 2 min. At the nanoscale, Yan *et al.* (2010) showed using X-ray energy-dispersive spectroscopy (XEDS), that nZVI particles are composed of a metallic-iron core surrounded by a thin disordered oxide layer (core-shell model). Only Hg⁰ could be observed with XPS at the nZVI surface confirming the possibility of Hg remediation by adsorption -

reduction. The authors obtained much lower removal efficiencies with a larger particle size of 4.1 μm .

As shown in the studies cited above, the removal of Hg^{2+} in aqueous media by metallic iron and/or magnetite proceeds with characteristic reaction times in the order of minutes. The characterization of the dynamics of aqueous Hg^{2+} reduction requires appropriate analytical tools with suitable time response. Monitoring these dynamics through time-resolved solution sampling or time-resolved Hg^0 gold-trapping is not convenient since it requires frequent ($\sim 0.1 - 1 \text{ min}^{-1}$) and numerous sampling and, therefore, a multiplication of analyses. Here, we used an automated mercury vapor analyzer based on atomic absorption with a sampling frequency of 0.2 min^{-1} to investigate the dynamics of Hg^0 production induced by the interaction between aqueous Hg^{2+} and the composite M/ZVI powder.

METHODOLOGY

Magnetite starting material

Magnetite starting material was synthesized from the corrosion of reagent grade iron beads (ZVI, Alfa Aesar – 00737, $\geq 99\%$, $2.8 \mu\text{m}$ diameter) at $200 \text{ }^\circ\text{C}$ in a 1 M solution of acetic acid in a stainless-steel autoclave. Temperature was measured to within $\pm 1 \text{ }^\circ\text{C}$ with a K-type thermocouple plunging in the solution. The reactor was stirred at 200 rpm. Pressure is used to monitor the reaction progress and measured with a pressure transducer. A total pressure increase $> 10 \text{ MPa}$ was measured which combined the effect of both heating and H_2 production associated with $3 \text{ Fe}^0 + 4 \text{ H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4 \text{ H}_2$ reaction. At the end of the experiment, the reactor was cooled at around $0.6 \text{ }^\circ\text{C min}^{-1}$. The run product was rinsed with ultrapure water, separated magnetically from the run solution, and dried at $50 \text{ }^\circ\text{C}$ for 24 h. Part of the product was placed on a double-sided carbon tape and carbon coated for imaging with scanning electron microscopy (SEM), another part is grinded under ethanol for X-ray powder diffraction. SEM image analysis performed on 150 particles from the run products yielded a mean particle size (and standard deviation) of $2.6 \pm 1.6 \mu\text{m}$ (Fig. 1). Quantitative X-ray diffraction using the BGMN software (Doebelin and Kleeberg, 2015) showed that the corrosion product is composed of magnetite with around 8 wt.% of residual Fe metal (Fig. S1). The BET surface area of the starting ZVI beads and of the experimental product was measured with N_2 gas and was found to be 0.4 and $9.0 \text{ m}^2 \text{ g}^{-1}$, respectively.

Titration experiments

Iron release from the M/ZVI product at constant pH (4 or 6) was measured by pH metric titration under N₂ bubbling using an automated titrator (716 Titrino, Metrohm) operated by Tiamo™ 2.3 software (Metrohm). Hundred and fifty milliliters of degassed NaCl solution at 10⁻³ M was adjusted at a fixed pH (4 or 6) with HCl. Then, 1.5 g of M/ZVI was added and the pH was maintained constant by automated addition of HCl (0.1 or 0.01 M, respectively). Both pH and volume of added acid were recorded. Aqueous iron concentration was determined on 2 mL solution samples. Magnetite particles were separated from the sampled solution with a magnet and the solution was centrifuged (5 min at 13000 rpm) and filtered to 0.025 μm. The aqueous Fe²⁺ and Fe_{tot} concentrations were derived using the o-phenanthroline spectrophotometric method (Herrera *et al.* 1989) at 511 nm with a spectrophotometer Lambda 35 Perkin Elmer. [Fe³⁺] was deduced from [Fe_{tot}] - [Fe²⁺].

Experimental set-up and Hg⁰ analyzer

The experimental set-up (Fig. S2) was composed of a 500 mL brown glass reactor in series with a 60 mL brown glass flask. The gas flux is monitored by a 0 - 325 ml min⁻¹ argon (Ar) glass-tube flow-meter placed upstream. The Ar tightness of the set-up was checked using a second flow-meter as outlet. All connections were made with fluoroethylen propylene (FEP) tubing to minimize gas adsorption and with silicone tubing at some points to ensure air tightness. The stirred glass reactor was closed tight with a screw cap equipped with a silicon/FEP septum. Three 3 mm in diameter holes were pierced in the septum to insert FEP tubes, themselves inserted into silicon tubes over the width of the septum. A first outlet was connected to a polycarbonate Luer shut-off valve to allow solution sampling. A second outlet was used for Hg⁰ outflow under Ar stream and was connected to the 60 mL condensation flask placed in an ice bath. The plug and the FEP and silicon tubes of the condensation flask through the silicon/FEP septum were designed similarly to those of the reactor but with two holes inside the septum for both Hg⁰ inflow and outflow. The outlet gas flow was filtered through a 60 mm Whatman® Vacu-Guard® 0.45 μm polytetrafluoroethylene (PTFE) inline membrane (Fig. S2) before it was analyzed by the Gardis device. The mercury analyzer cycle started with pumping the Ar gas for 90 s. Elemental Hg accumulated on two 99.99% pure gold traps following a ‘dual amalgamation’ process which was selective to Hg⁰. Followed a thermo-desorption stage which lasted 60 s at 10 mL min⁻¹ using a Ni-Cr wire wrapped around the gold trap for heating. The desorbed Hg⁰ passed through a two-optical beam for absorption measurements at 254 nm. At the end of the measurement cycle, a cooling step of 2 min was applied during which the analyzer was bypassed and the gas was then directed to the external gold trap. Operating conditions were optimized to obtain (i) the maximum Hg⁰ flow inside the analyzer and avoid the reactor to be under pressure

and (ii) the highest Hg^0 sensitivity when the lowest volume (0.2 μL) of Hg^0 saturated vapor was injected for calibration. With an input Ar flow rate of 75 mL min^{-1} , the gas sampling flow rate was tuned to around 52 mL min^{-1} for a sampling time of 90 seconds. It should be noted that with an inflow rate of 75 mL min^{-1} , the gas contained in the headspace of the reactor was renewed every 2-3 minutes.

The sample powder was reacted with 300 mL of a Hg^{2+} solution under stirring with a magnetic bar. The reactor was equipped with a glass bubbler to ensure fine Ar inflow into the solution. The outlet gas flow was analyzed every 5 min using a cold vapor - atomic absorption spectrometry (CV-AAS) automated Mercury analyzer (Gardis-5[®]). This type of analyzer is able to detect down to 0.5 pg Hg^0 vapor (Urba *et al.* 1995). The gas which did not flow through the Gardis-5[®] analyzer was collected in a sandy gold trap for further analysis using CV-AFS (see next section).

Hg^0 background signal was collected in a set of blank experiments as well as at the beginning of all experiments prior to the powder sample injection. The Gardis baseline (~ 1 to 3 pg) was first determined using pure water and by monitoring Hg^0 in the set-up using the same experimental conditions as for all other experiments (90 second sampling, Ar inflow rate 75 mL min^{-1}).

Complementary Hg analyses

Elemental Hg that was not sampled (and analyzed) with the Gardis-5[®] device, *i.e.*, mainly during the Gardis-5[®] cooling stage of 2 min, was trapped on an external sandy gold-trap (Fig. S2). The Hg^0 trapped on the external gold-trap was desorbed on the day the experiment ended in a pre-cleaned (500°C, 1h) opaque flask containing 10 mL of 5 mM KMnO_4 ($\text{Hg} < 0.000005\%$) in 5 % pure HNO_3 (Optima[™], $\text{Hg} < 50\text{ pg g}^{-1}$). Desorption was achieved by repeated heating (10 times) of the external gold trap according to cycles of 13 seconds using an induction coil under a flow of 99.999 % Ar gas. Hg content of the KMnO_4 solution was further quantified using a CV-AFS with a protocol based on BrCl oxidation, SnCl_2 reduction, Hg^0 amalgamation and detection by atomic fluorescence at 254 nm with a detection limit of 0.1 ng L^{-1} .

Additional Hg remaining in the system, either in the solution, adsorbed onto the residual powder or onto the reactor walls as well as aqueous Fe^{2+} , were quantified in selected experiments. Samples for Hg analysis were stored in acid-cleaned FEP Teflon bottles following ultra-clean techniques (Bloom, 1995), acidified with Rotipur[®] HCl ($\text{Hg} < 50\text{ ng L}^{-1}$) and kept at 4 °C until analysis.

Recovered solutions were acidified at 0.5 % (v/v) (Parker & Bloom 2005). A 1 mL aliquot was complexed with 2 mL of a pH 4.5 buffer and 2 mL of 6.0 10^{-3} M o-phenantroline for Fe^{2+}

quantification. Hg adsorbed on the sample powder and on the gas frit was recovered by leaching both magnetic stirrer bar and gas frit in 50 % (v/v) HCl under ultrasonic bath for 30 min. The Hg contribution of acid and glassware was determined using the same conditions of leaching in ultra-pure water. Reactor walls were reacted with 300 mL of 10 % (v/v) HCl for at least 24 h, and the recovered solution was analyzed for Hg after filtration through polyvinylidene difluoride 0.45 μm membranes.

The pH of the reacting Hg solution was determined with a Metrohm 781 pH-meter at the beginning (*Start pH*, Table 1) and at the end of the experiments (*End pH*, Table 1). In Run 2-7, pH was measured with the pH meter of the automated titrator. For the *Start pH* measurement, the solution was sampled several minutes after the beginning of the experiment, *i.e.*, when the Ar inflow had begun and the sample powder had not yet been introduced. The experiment was considered to start at t_0 when the sample was introduced.

RESULTS

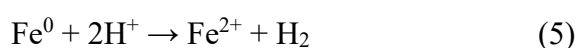
M/ZVI dissolution kinetics at pH 4 and 6 from HCl titration

Titration of M/ZVI was performed at pH 4 which has been the starting pH for most monitoring experiments of Hg^0 production. The volumetric HCl addition followed three main steps (1, 2 and 3 on Fig. 2). First, around $4 \cdot 10^{-3}$ mole HCl was introduced within 1 hour ($4 \cdot 10^{-3}$ mole h^{-1}). Then, automated HCl addition rate decreased down to $2.3 \cdot 10^{-3}$ mole h^{-1} . After 5.5 hours of titration, automated HCl addition mostly stopped (Step 3). Overall, a total of $1.2 \cdot 10^{-2}$ moles of HCl was added.

A similar succession of steps could be inferred from the evolution of $[\text{Fe}^{2+}]$ in the solution (Fig. 2). After 19 hours, a total of $5.8 \cdot 10^{-3}$ mole of iron has been released into the solution corresponding to a ca. 2:1 molar ratio between added HCl and Fe^{2+} ,aq as expected from electroneutrality:



The amount of aqueous Fe^{3+} was around 2 orders of magnitude less concentrated than Fe^{2+} . X-ray diffraction of the residual powder after titration indicated that all ZVI was consumed. The amount of aqueous Fe^{2+} after Step 1 of $4 \cdot 10^{-3}$ mole (Fig. 2) roughly corresponds to the number of moles of Fe^0 in the solid sample. Therefore, Step 1 can be attributed to the anoxic dissolution of ZVI at rate of $2 \cdot 10^{-3}$ mole. h^{-1} (pH = 4):



Automated titration of the M/ZVI product has also been performed at pH 6 over 26 hours (Suppl. Figure S3). Dissolution was by two to three orders of magnitude slower than at pH 4 and occurred in a discontinuous manner (Fig. S3). In a first step (Zone 1, Fig. S3), HCl was added at a maximum rate of ca. $1.5 \cdot 10^{-5}$ mole.h⁻¹ within the first two hours. This first step was followed by a second step with almost no HCl addition (Zone 2) which finally resumed after three hours (Zone 3) at a rate of $0.5 \cdot 10^{-6}$ mole.h⁻¹ until the titration was terminated at $t_0 + 25$ h. At $t_0 + 19$ h, the solution was sampled and contained only $7.0 \cdot 10^{-6}$ mole of Fe²⁺ corresponding to the anoxic dissolution of only 260 mg per kg of ZVI. X-ray powder diffraction of the residual M/ZVI powder after the experiment confirmed that most of the initial ZVI was still present. The Cl⁻/Fe²⁺ molar ratio in the solution was close to 1.6 and therefore departed from the expected ratio of 2 as predicted by Eq (4). This discrepancy is not accounted for by the presence of aqueous ferric iron which was not present in significant amount since $[\text{Fe}^{2+}] \sim [\text{Fe}_{\text{tot}}]$.

Patterns of Hg⁰- Gardis production events and effect of pH

A total of five blank experiments was carried out which are detailed in the supplementary data. These blanks showed that neither ZVI nor M/ZVI was an intrinsic source of Hg²⁺. Therefore, any Hg⁰ production event that would occur after sample introduction corresponded to mercury that came from the solution. They also demonstrated that NaN₃ cannot be at the origin of measured Hg⁰ production events. Furthermore, aqueous Fe²⁺ was not found to produce Hg⁰ in the 2.3 - 9 pH range. Small Hg⁰ production events (< 10 - 15 pg) were associated with NaOH addition which occurred to contain minor Hg.

Besides these blank experiments, time-resolved Hg⁰ production was monitored during the reaction of M/ZVI with Hg²⁺ solutions, prepared from HgCl₂ or Hg(NO₃)₂, with concentrations between 20 and 40 ng L⁻¹ (Table 1). Various patterns of Hg⁰ production events were recorded which appeared to be strongly dependent on the pH evolution in the course of each experiment.

Experiment 2-1 (*start pH* = 4.2) was the only experiment that was performed with NaN₃ (pKa = 4.6, 10 mM) which is a bacterial activity inhibitor (Hochstein *et al.* 1988; Ingledew *et al.* 1984; Hendrix *et al.* 2019). The idea was to test whether the Hg⁰ production events could relate to bacterial activity. In the course of Run 2-1, pH only varied within the 4 – 5 range due to the buffering effect of NaN₃. The Hg⁰ - Gardis production pattern of Run 2-1 (Figure 3A) was characterized by a strong Hg⁰ production event which occurred 37 min after the M/ZVI sample was dropped into the reactor. This event led to the reduction of around half of the initial Hg²⁺_{aq} and was not related to bacterial activity.

Another typical Hg^0 production pattern was encountered in M/ZVI experiments to which no NaN_3 was added and for which pH drifted to values above 6 in the course of the measurements. For example, Run 2-2 showed a sharp Hg^0 production peak (Figure 3B) about 22 min after the introduction of M/ZVI, followed after around 8.5 hours by a second main Hg^0 production peak which spread over around 10 h. This typical pattern with a first Hg^0 production peak followed by a wide (and sometimes multiple) peak was basically encountered in every experiment where the *End pH* was above 6. It should be noted that the second reduction event did not always occur at the same time in the course of the experiment.

In order to relate Hg^0 production to pH evolution, both parameters were simultaneously monitored in Run 2-7 (Figure 3D). A first Hg^0 production event was observed in the form of a shoulder on the main Hg^0 production peak, immediately after M/ZVI was dropped in the reaction flask. Within less than an hour, pH increased to its maximum value (pH \sim 8.5). The maximum Hg^0 production rate coincided with the pH maximum. The slow pH decrease observed after aqueous Hg^{2+} had been reduced can be related to the slow oxidation of aqueous Fe^{2+} due to the flow of Ar gas which contained around 5 ppmv of O_2 . Indeed, in 10 h, an O_2 contamination of *ca.* 10^{-5} mole per liter of solution can be calculated which is of the same order of magnitude as the $[\text{Fe}^{2+}]$ in the recovered solution (Table 1). In the early stage of the experiments, however, while ZVI was still present in the solid starting material, reducing conditions might have prevailed as imposed by the dissolution of ZVI (named Fe^0 in R.6) which can potentially consume O_2 :



Effect of single-phase ZVI on Hg reduction dynamics

In order to decipher the specific role of ZVI in the composite M/ZVI powder with respect to Hg^{2+} reduction, Hg^0 monitoring experiments were carried out independently with single-phased ZVI (Run 2-9, 2-11, 2-11bis). We used as starting material the ZVI compound (Alfa Aesar – 00737, \geq 99%) from which M/ZVI was synthesized. In all reduction experiments with ZVI, Hg^0 production was significant and observed shortly after ZVI introduction, in the form of a sharp Hg^0 - Gardis peak. After each Hg^0 production event, $[\text{Fe}^{2+}]$ and pH (from 5.2 to 7.9 in Run 2-11; from 5.9 to 7.8 in Run 2-11bis) both increased.

Run 2-11 and 2-11bis were both performed by changing some of the experimental parameters in the course of the experiment itself taking advantage of the real-time monitoring of the Hg^0 production allowed by the Gardis analyzer. In 2-11, *start pH* was adjusted to 3.9 and 10.6 mg of

ZVI were introduced at t_0 in the $25 \text{ ng L}^{-1} \text{ Hg}^{2+}$ solution. After the first event of Hg^0 production, a pH of around 5.2 was measured ($t_0 + 18.4 \text{ h}$) and $[\text{Fe}^{2+}, \text{aq}]$ reached 0.31 mg L^{-1} ($t_0 + 18 \text{ h}$) meaning that around 1 wt.% of the ZVI had been dissolved. Further addition of 11 mg of ZVI ($t_0 + 19.1 \text{ h}$) did not lead to further Hg^0 production confirming that the amount of available ZVI was not the limiting factor to Hg^0 production. The addition of 25 ng L^{-1} of Hg^{2+} to the solution ($t_0 + 22.7 \text{ h}$) triggered a sharp and intense Hg^0 - Gardis peak (*ca.* 400 pg) at pH around 5.2.

We show here that in the conditions of the 2-11 experiment with 10 mg of ZVI, the extension of the Hg^0 production event is limited by the amount of Hg^{2+} and not by the amount of ZVI since ZVI addition does not lead to another Hg^0 production event. The corresponding reduction process was effective and fast at pH 4 and 5.2 (2 h and 2.5 h, respectively). The anoxic dissolution of ZVI can drive the pH to values up to 8 as measured at $t_0 + 42 \text{ h}$, *i.e.*, at the end of the 2-11 experiment.

The 2-11bis experiment was basically similar to the 2.11 one but higher pH was investigated. The starting pH was adjusted to 6.6 and 10.5 mg of ZVI was added at t_0 . Hg^0 was produced immediately as recorded on the Gardis device in the form of the sum of two overlapping peaks. At $t_0 + 23 \text{ h}$, pH reached 8.5 and another 25 ng.L^{-1} of Hg^{2+} was added to the solution which immediately resulted in a major Hg^0 - Gardis production peak (*ca.* 500 pg amplitude). pH was then decreased down to 5.4 and another 25 ng.L^{-1} of Hg^{2+} was added ($t_0 + 28 \text{ h}$) and, again, a major Hg^0 - Gardis event was recorded with *ca.* 400 pg of amplitude.

Effect of single-phase magnetite on Hg reduction dynamics

The specific role of magnetite in the Hg^{2+} reduction process has been tested on the M/ZVI product after complete removal of its ZVI component by selective dissolution. The dissolution of ZVI which is far more soluble than magnetite, was achieved in the experimental setup itself in order to avoid unnecessary handling and associated contamination/oxidation. In the 2-12 experiment (Fig. 3E), 12.3 mg of the M/ZVI product was introduced in the reactor containing a Hg-free solution at pH 4.3. The pH rise which was associated to the selective dissolution of the ZVI component, was compensated by successive additions of HNO_3 until pH did no longer increase and remained equal to 4.3. This constant pH regime was interpreted as the complete dissolution of the ZVI component. At this stage, $[\text{Fe}^{2+}]$ reached 6.5 mg L^{-1} . This concentration is actually higher than expected in the case of the dissolution of all ZVI (8 wt.%) contained in the starting M/ZVI, partial dissolution of the magnetite component must thus also be considered. At $t_0 + 28 \text{ h}$, Hg^{2+} was added to reach a concentration of 25 ng L^{-1} in the reactor. A small and sharp Hg^0 production event was then recorded (amplitude *ca.* 10 pg). This type of small amplitude event was systematically recorded when Hg^{2+} was added to the experimental solution and likely reflects an increase of the Hg^0 partial pressure

according to Henry's law. Then, pH was increased to 6.3 what triggered a large Hg^0 production event which lasted around 10 hours. Once the Hg^0 - Gardis signal returned below 2 pg, pH was 5.6 and another 25 ng.L^{-1} of Hg^{2+} was added. This, again, triggered Hg^0 production, indicating that the previous Hg^0 production steps consumed all the Hg^{2+} that was available for reduction.

Magnitude of the Hg reduction

The proportion of initial Hg that is reduced and trapped on both Gardis and external gold trap has been determined for a selection of experiments (Table 2) and was found to amount to around 40 – 50%. The amount of Hg^{2+} that remained in the solution at the end of the experiment was typically comprised between 5 and 15 %. Since particles can be sampled with the solution which was not filtrated, this proportion should be seen as an upper bound of the final $[\text{Hg}^{2+}]$. Indeed, it can be noted that the solution of Run 2-12 which has been filtrated displays the lower Hg content ($[\text{Hg}^{2+}]_{\text{end}}$, Table 1). The Hg adsorbed onto both residual solid sample and gas frit was found to represent another 30% of the initial Hg (Table 2). Finally, part of the Hg adsorbed onto the flask walls to a level of ca. 15% as determined on the 2-12 experiment.

DISCUSSION

Limitations of the set-up for monitoring aqueous Hg^{2+} reduction

The experimental set-up that was designed in this study allowed the identification of Hg^0 production events that typically proceeded at the hour timescale. The frequency of the Hg^0 analysis with the Gardis-5[®] (0.2 min^{-1}) allowed a good resolution of these Hg^0 production events. It can thus be concluded that the set-up is well-suited to investigate the Hg^0 production dynamics by magnetite- and ZVI-based materials. At this stage, however, the Hg^0 - Gardis measurement does not provide an accurate evaluation of the total Hg^0 that is produced in the experiments. The proportion of total Hg^0 that was trapped and analyzed by the Gardis device could basically vary by a factor of two from one experiment to another although it should be reproducible for identical sampling procedure and gas flow rate. Possible variations in Ar gas flow might be invoked, either Ar inflow variations in the whole system or in the gas analyzer upon automatic pumping. Therefore, only the order of magnitude of the total Hg^0 produced could be inferred at this stage and Hg^0 - Gardis data can only be considered as a semi-quantitative estimate of the total amount of Hg^0 that was actually produced.

Being aware of that limitation, we show here that the composite powder obtained from the corrosion of iron metal powder and consisting in a mixture of magnetite (M) and residual iron metal (ZVI) was effective to reduce aqueous Hg^{2+} in the 4 – 8.5 pH range. The sensitivity of the Gardis analyzer made it possible to probe Hg^0 production at the picogram level. In order to avoid memory effects on the Gardis analyzer encountered when Hg^0 exceeds amounts in the order of 160 pg, the mass of starting M/ZVI was minimized down to a level (ca. 10 mg) at which it could still be accurately weighed and an initial $[\text{Hg}^{2+}]$ of 25 ng L^{-1} was chosen. The quantity of Hg adsorption sites on the surface of magnetite in the present experiments was close to 6 nmole of sites per liter considering an adsorption site density at the surface of Fe_3O_4 of ca. $3.5 \cdot 10^{-5} \text{ mole m}^{-2}$ (e.g., Wesolowski *et al.* 2000; Missana *et al.* 2003). This concentration of adsorption sites is to be compared to the $[\text{Hg}^{2+}]$ which amounts to around 125 pmole.L^{-1} in our experimental solutions. For comparison, in their $\text{Hg}^{2+}_{\text{aq}}$ reduction experiments with magnetite, Wiatrowski *et al.* (2009) used a site concentration that was only two times higher and around 80 nmole.L^{-1} of aqueous Hg^{2+} could be reduced. Therefore, the Hg reduction investigated here proceeded at only a few percent of the reduction capacity of magnetite present in M/ZVI. The $[\text{Hg}^{2+}]$ was thus the limiting factor of Hg^0 production as confirmed by its reactivation after Hg^{2+} addition in Run 2-12. Similarly, Hg^0 production in experiments performed with ZVI as starting material were also limited by the amount of aqueous Hg^{2+} (Run 2-11 and 2-11bis).

Preliminary tests on solutions containing $[\text{Cl}^-]$ comprised between 2 and 5 mmole.L^{-1} (not shown here) with initial $[\text{Hg}^{2+}]$ of 25, 75, 375 ng.L^{-1} and a M/ZVI mass of 10.1, 10.8 and 2.1 mg yielded a total Hg^0 production of 1020, 3320 and 4300 pg, respectively, showing a relatively good proportionality between produced Hg^0 and both initial quantity of M/ZVI and $[\text{Hg}^{2+}]$.

Dynamics of aqueous Hg^{2+} reduction by M/ZVI

Titration experiments have shown that the dissolution of M/ZVI released aqueous iron which tended to increase the pH of the host solution. At pH 4 which was the starting pH of most Hg^0 monitoring experiments, ZVI was found to dissolve preferentially. At pH 6, the dissolution rate of M/ZVI was three orders of magnitude slower. When transposed to the Hg^0 monitoring experiments where pH was not buffered (apart for Run 2-1 containing NaN_3), it is thus expected that the pH increase due to M/ZVI dissolution will slow down with time until it reaches its final value.

$[\text{Fe}^{2+}]$ at the termination of all experiments was found to vary between 2.5 and 4 mg.L^{-1} corresponding to a mass of dissolved iron of around 0.7 to 1.1 mg, *i.e.*, between 7 and 11 wt.% of the starting material. Since ZVI represented around 8 wt.% of the starting material and since titration data at pH 4 showed that ZVI dissolved preferentially, it can be concluded that (1) the main

contribution to the pH increase was the anaerobic dissolution of ZVI through the production of hydroxide ions ($\text{Fe}^{\circ}_{\text{solid}} + 2 \text{H}_2\text{O} \Rightarrow \text{Fe}^{2+}_{\text{aq}} + \text{H}_2 + 2 \text{OH}^-$) and (2) all the ZVI in the starting material might have been consumed in our experiments.

The decrease in dissolution rate with increasing pH has been reported for both ZVI (Fu *et al.* 2014) and magnetite (Missana *et al.* 2003). In particular, Fu *et al.* (2014) indicated that iron release into the solution by ZVI particles becomes limited by the formation of a passivating hydroxide shell. Wilkin & McNeil (2003) have investigated the rate of removal of a series of heavy metals by ZVI at pH 2.3 and 4.5. They also observed an overall pH increase associated with ZVI dissolution. Actually, they could not define the removal rate for Hg since all the initial Hg^{2+} had already been removed from the solution before their first $[\text{Hg}^{2+}_{\text{aq}}]$ measurement. This type fast kinetics is consistent with our observation for Hg^{2+} reduction by ZVI.

Experiments with pure ZVI yielded a Hg^0 - Gardis production pattern that was composed of a single event which could occur in a range of pH from 4 to 8.5 and possibly down to 2 according to Run 2-3 (Fig. 3C).

By comparison, single phase magnetite did not reduce $\text{Hg}^{2+}_{\text{aq}}$ at pH 4.3 (Run 2-12) which was the starting pH of most experiments presented here. The production of Hg^0 by magnetite was triggered by the increase of pH up to 6.5 as attained in most experiments in response to ZVI dissolution mainly. We thus conjecture that Hg^0 - Gardis patterns displaying two successive Hg^0 production events are the sum of the Hg^{2+} reduction by ZVI followed by the reduction of remaining Hg^{2+} at mild acidic pH.

The pH dependency of Hg reduction kinetics by stoichiometric magnetite has been established by Wiatrowki *et al.* (2009). The expected reduction rate for our experimental parameters have been calculated with their data and are displayed in Figure 4 in the form of $\text{Hg}^0 = f(t)$ curves. It can be clearly seen (Figure 4) that at pH below 5, the Hg^0 production rate is associated with a broad peak of low intensity that will be barely resolved by the Gardis monitoring. At pH 6.5, a sharper Hg^0 - Gardis peak should be produced with Hg^{2+} reduction that proceeds within a few hours in good agreement with our observations.

Therefore, the respective role of the two components of the M/ZVI product with respect to Hg^{2+} reduction can be summarized as follows. First, at pH 4, Hg^{2+} is partly reduced to Hg^0 by ZVI which, in addition, shifts the pH of the solution to mild acidic values at which the Hg^{2+} reduction rate by magnetite allows to further reduce Hg^{2+} within a few hours.

The process of Hg reduction by ZVI in the form of nanoparticles is described as a core-shell model which involves Hg^{2+} sorption onto an iron hydroxide shell which covers the nanoparticle and the reduction of Hg^{2+} into Hg^0 by electron transfer from the ZVI core across the shell (Yan *et al.* 2010). This shell with a thickness from a few nanometers to 25 nm is commonly observed on ZVI

nanoparticles (e.g., Yan *et al.* 2010; Crane *et al.* 2015). As expected for a surface-controlled process, Yan *et al.* (2010) showed that the Hg reduction rate decreases with ZVI particles having lower surface area. Martin *et al.* (2008) showed that the complete oxidation of nanoparticles of ZVI (50 – 100 nm) by aqueous Cu^{2+} under near anoxic conditions produces an iron oxide-hydroxide shell of around 3 nm. The reactivity of the nanoparticle is bounded to the thickness of the shell that can become passivating with respect to the core-shell reduction process (e.g., Wang *et al.*, 2010). However, in the experiments performed here where ZVI dissolves and where pH increases consecutively, passivation might not be efficient since iron is continuously released into the solution. The dissolution rate of iron decreases with pH, as observed here at pH 6 compared to pH 4. Passivation by an oxide/hydroxide layer may then become relevant towards circumneutral pH. Actually, the stepwise dissolution of ZVI contained in M/ZVI observed at pH 6 in titration experiments (Fig. S3) could reflect the competition between passivation and dissolution. Such discontinuous dissolution implies that from pH 6 and above, the rate of pH increase is variable. This explains also why the second Hg^0 event which is attributed to magnetite once pH exceeds 6, occurs at different times in our experiments.

Whereas anaerobic dissolution of ZVI imposes reducing conditions (Sun *et al.* 2006), progressive decrease of the iron dissolution rate due to increasing pH will favor, in the presence of oxygen, the precipitation of iron oxide and/or hydroxide possibly as a shell around ZVI. The slow pH decrease observed on Fig. 3D (Run 2-7) is the likely result of iron oxide/hydroxide slow precipitation due to the presence of O_2 as traces in the Ar gas. Actually, the presence of magnetite once circumneutral conditions have been attained will ensure that fast and efficient Hg^{2+} reduction will proceed. A fraction of this magnetite can actually be produced by anaerobic corrosion of the ZVI (e.g., Odziemkowski *et al.* 1998) according to the same process that led to the hydrothermal production of the M/ZVI product from ZVI.

The pseudo-first order rate law established by Wiatrowski *et al.* (2009) for Hg reduction in the presence of Fe_3O_4 and its pH dependency are found to apply even to Hg solutions that are around 1000 times less concentrated than those used by the authors to establish their rate law. We showed that even at a Hg^{2+} concentration of $25 \text{ ng}\cdot\text{L}^{-1}$ which is about 100 times below the maximum contamination level in drinking water recommended by the US environmental protection agency, $30 \text{ mg}\cdot\text{L}^{-1}$ of M/ZVI is able to remove around 50 % of this Hg by reduction into Hg^0 in addition to the fraction that was adsorbed onto the reactor walls and onto the M/ZVI product itself. Although much less soluble and less sensitive to oxygen than ZVI, magnetite can oxidize what potentially lowers the reduction rate of contaminants (Gorski *et al.* 2010). The higher reactivity of ZVI may prevent or delay magnetite oxidation by imposing anoxic conditions.

CONCLUSION

Both ZVI and magnetite surfaces have the chemical ability to reduce aqueous Hg^{2+} into Hg^0 . However, the use of these compounds for Hg^{2+} remediation in aqueous environments faces some intrinsic limitations. ZVI can lose its Hg^{2+} reduction efficiency upon dissolution or surface oxidation, two processes that are likely to occur rapidly owing to the high metastability of ZVI. Magnetite on the other hand is chemically more stable. However, magnetite powders with surface area in the 5 - 100 $\text{m}^2\cdot\text{g}^{-1}$ range are costly to produce at the industrial scale. The use of composite M/ZVI powders in acidic to mild acidic polluted waters and possibly aqueous industrial wastes, may offer an interesting alternative to the use of either of its constitutive components alone. This is especially the case under acidic conditions under which the ZVI component reduces efficiently part of the Hg^{2+} . At the same time, the ZVI dissolves, thus shifting the pH above 6. At $\text{pH} > 6$, the kinetics of Hg^{2+} reduction by magnetite becomes optimal and magnetite takes over the reduction of Hg^{2+} . Indeed, the rate of aqueous Hg^{2+} reduction by magnetite is actually 9 times faster at pH 6.5 than at pH 4 (Wiatrowski *et al.* 2009). Therefore, a pH shift from 4 to 6.5 may allow the use of 9 times less magnetite to achieve the same Hg^{2+} removal rate. At constant magnetite mass, a magnetite product with a 9-fold lower specific surface area can be used, e.g. grains with a diameter of 200 nm instead of 25 nm..

The low-temperature hydrothermal process that was applied here to commercial Fe^0 for the synthesis of M/ZVI could also be applied to ZVI-based wastes from the steel industry in order to minimize the cost of the starting raw material. The M over ZVI ratio can be easily tuned by varying the duration of the production process. The obtained products can be tested with the experimental set-up developed here which consists in the online Hg^0 analysis of the gas bubbling in a simple glass reactor containing solutions with sufficiently low $[\text{Hg}^{2+}]$ to remain harmless for the operator. It must be noted that further Hg^0 removal can be envisaged using available technology for elemental mercury capture from flue gas, some of them being based on materials prepared from by-products of the steel industry as well (Ma *et al.* 2019). The next step should be the investigation of the M/ZVI potential for Hg remediation in polluted soils. Indeed, the Hg^0 production kinetics observed here are not directly applicable to soils where mercury is expected to be strongly retained in the solid fraction (Liao *et al.* 2009) in particular in the presence of organic matter (Yin *et al.* 1997a, Yin *et al.* 1997b, Miretzky *et al.* 2005).

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FIGURES

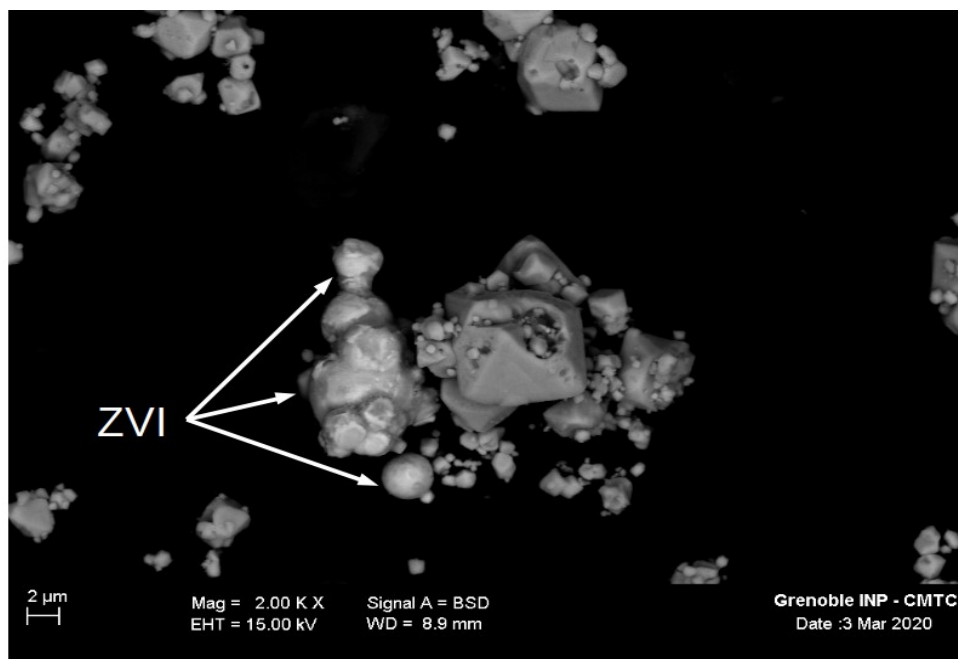


Figure 1: Back-scattered electron image of the M/ZVI product. Euhedral magnetite grains have sizes comprised between a few hundreds of nm to almost 10 μm . Residual ZVI beads are indicated by arrows on the SEM image.

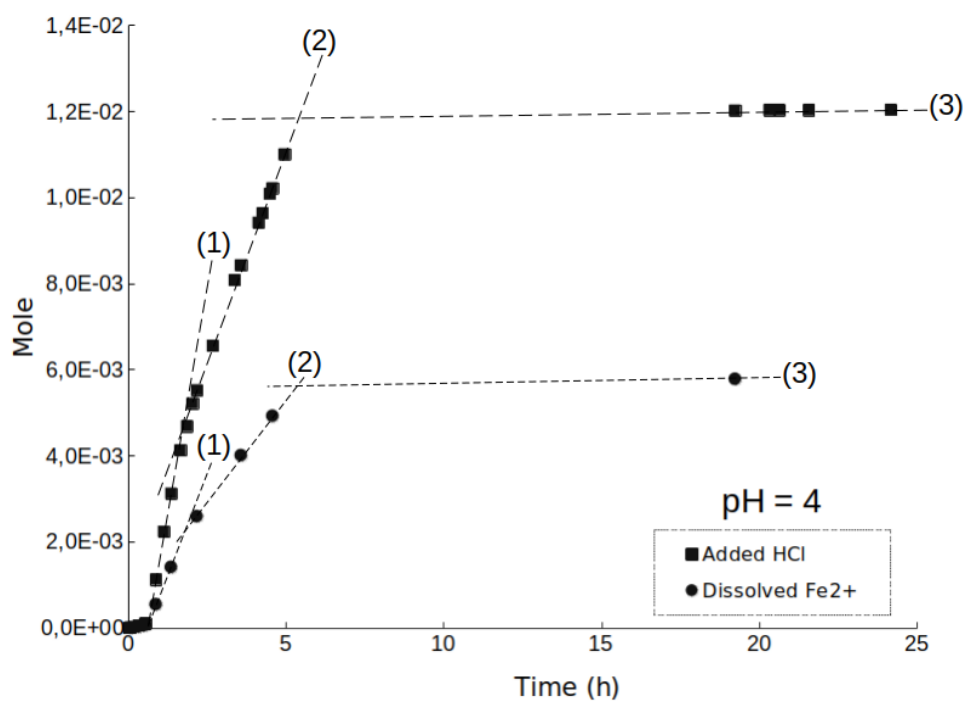


Figure 2: pH-metric titration of the M/ZVI product and iron release rate. pH was set to 4 and the titration was performed using 0.1 M HCl. Upper curve corresponds to added HCl moles and black dots are [Fe²⁺] data. Three successive dissolution steps can be distinguished, labeled (1), (2) and (3).

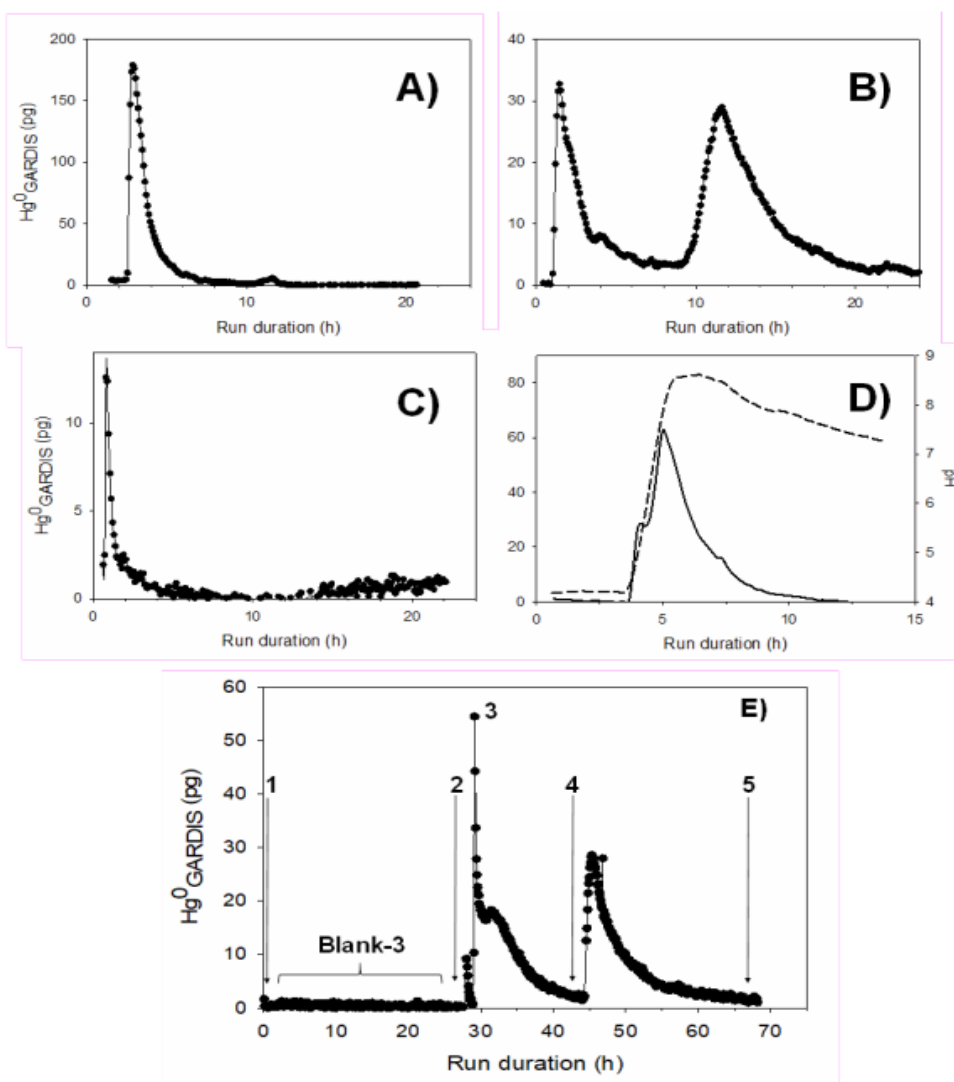


Figure 3: Typical Hg^0 - Gardis production pattern. **(A)** Run 2-1 in a 10^{-3} M NaN_3 solution, **(B)** Run 2-2 where pH drifted to a value above 6 in the course of the experiment, **(C)** Run 2-3 at pH of *ca.* 2 after addition of $1.5 \cdot 10^{-3}$ mole HNO_3 . **(D)** Run 2-7 with time-resolved Hg^0 - Gardis (plain curve) and pH monitoring (dashed curve). **(E)** Run 2-12 with selective ZVI dissolution to investigate single-phase magnetite behavior. At Point 1, pH was adjusted to 4.3 and 12.3 mg of M/ZVI was added. pH was maintained at 4.3 by HCl addition until ZVI dissolution. Once pH did no longer increase, Hg was added to 25 ng L^{-1} (Point 2) which produced a small Hg^0 peak that was always encountered after Hg^{2+} addition. The Hg^0 - Gardis production peak at Point 3 occurred after the pH was increased from 4.3 to 6.3. pH decreased down to 5.7 as measured at Point 4 at which 25 ng L^{-1} of Hg was added again. At Point 5, pH was still 5.7.

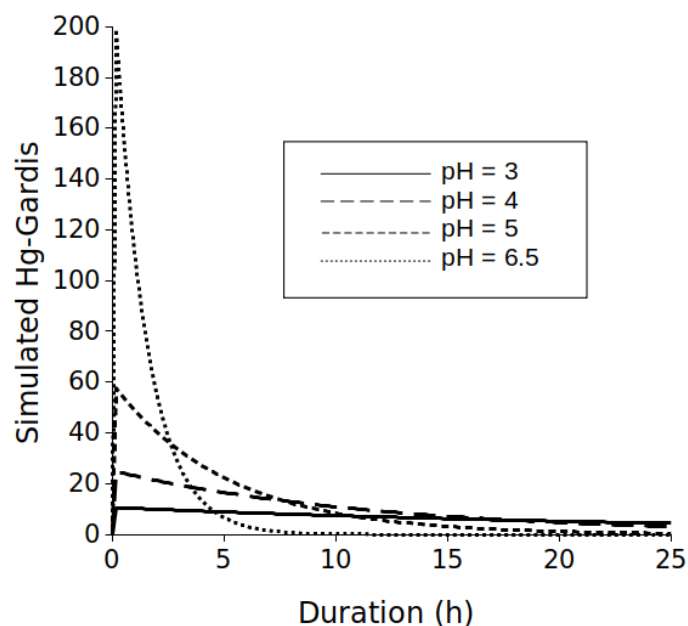


Figure 4: Simulation of Hg^{2+} reduction kinetics by magnetite as a function of pH using the kinetics law by Wiatrowski *et al.* (2009). Total amount of $[\text{Hg}^{2+}_{\text{aq}}]$ reduced and trapped on the Gardis is set to 6 ng.L^{-1} for the simulation.

TABLES

Run	Reactor type	Start pH	End pH	Duration (h)	m start. mat. (mg)	$[\text{Fe}^{2+}]$ (mg L ⁻¹)	H ₂ O vol. (ml)	$[\text{Hg}^{2+}]$ start (ng/l)	$[\text{Hg}^{2+}]$ end (ng/l)	Tot. Hg ⁰ (pg)
M/ZVI										
2_1*	1	4.16	4.8	20.4	10.3	3.8	285.3	28.8	7.4	3553
2_2	1	4.2	6.1	68.7	10.3	2.5	289.1	27.8	3.4	4142
2_3	1	2.1	2.2	22.0	10.3	3.6	287.1	25.4	2.3	704
2_4	1	3.7	7.9	21.4	10.1	0.2	289.6	24.6	2.2	11547
2_5	1	5.1	7.4	47.9	10.7	0.2	291.2	24.1	1.3	2872
2_6**	1	4.2	7.0	21.4	10.6	1.5	284.3	23.8	0.6	3336
2_7	2	4.2	6.8	23.9	10.5	2.1	300.8	23.6	0.8	3326
2_8	2	4.1	4.2	23.0	0.0	n.d.	302.1	n.d.	n.d.	n.d.
2_12	1	4.4	5.7	68.2	12.3	5.2	280.2	40.5	0.3	4589
ZVI										
2_9	2	4.2	6.8	19.4	1.4	3.0	298.6	23.8	3.2	2658
2_11	1	3.9	8.0	41.9	21.6	2.9	290.7	n.d.	n.d.	n.d.
2_11bis	1	6.6	7.5	28.0	10.4	0.7	274.5	n.d.	n.d.	n.d.
2_13	1	4.6	6.4	16.7	10.4	0.5	285.5	n.d.	n.d.	n.d.

Footnote: *with NaN_3 (10^{-3} M); ** Hg supplied as $\text{Hg}(\text{NO}_3)_2$

Table 1: List of experiments with online monitoring of the Hg^0 production. Reactor type: (1) Opaque glass flask (592 ml); (2) Transparent glass wrapped in Al foil (547 ml).

Run	Hg ⁰ -GARDIS (pg)	Hg ⁰ -Trap (pg)	Magnetite (pg)	Reactor wall (pg)	Recovery (%)
2_2	2080	2062	1762	n.d.	85
2_9	668	1990	2174	n.d.	81
2_12	3709	880	2258	1975	78

Table 2: Hg distribution in selected experiments. The recovery (%) is defined as the total Hg after the experiment divided by the total Hg introduced in the system initially. Note that the solution of Run 2-12 has been filtrated and thus Hg associated with the filtrated particles is not accounted for by in the recovery.

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TITLE: REAL-TIME MONITORING OF AQUEOUS Hg²⁺ REDUCTION DYNAMICS BY MAGNETITE / IRON METAL COMPOSITE POWDERS SYNTHESIZED HYDROTHERMALLY

Brunet et al.

SUPPLEMENTARY MATERIAL

1. X-Ray diffraction of the starting material

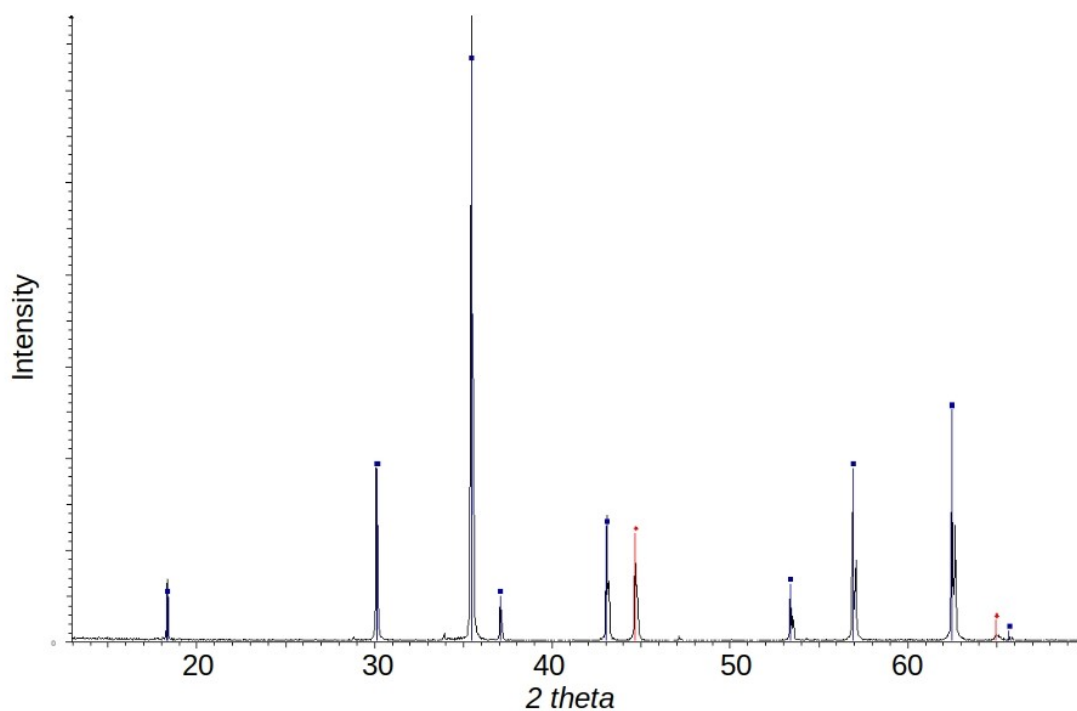


Fig. S1: X-Ray powder diffraction pattern of the M/ZVI product. Magnetite reflections are in blue and ZVI reflections in red. Rietveld refinement of the diffraction pattern yielded 8 ± 2 wt.% ZVI in the M/ZVI product used in the experiments presented here.

2. Description of the experimental set-up

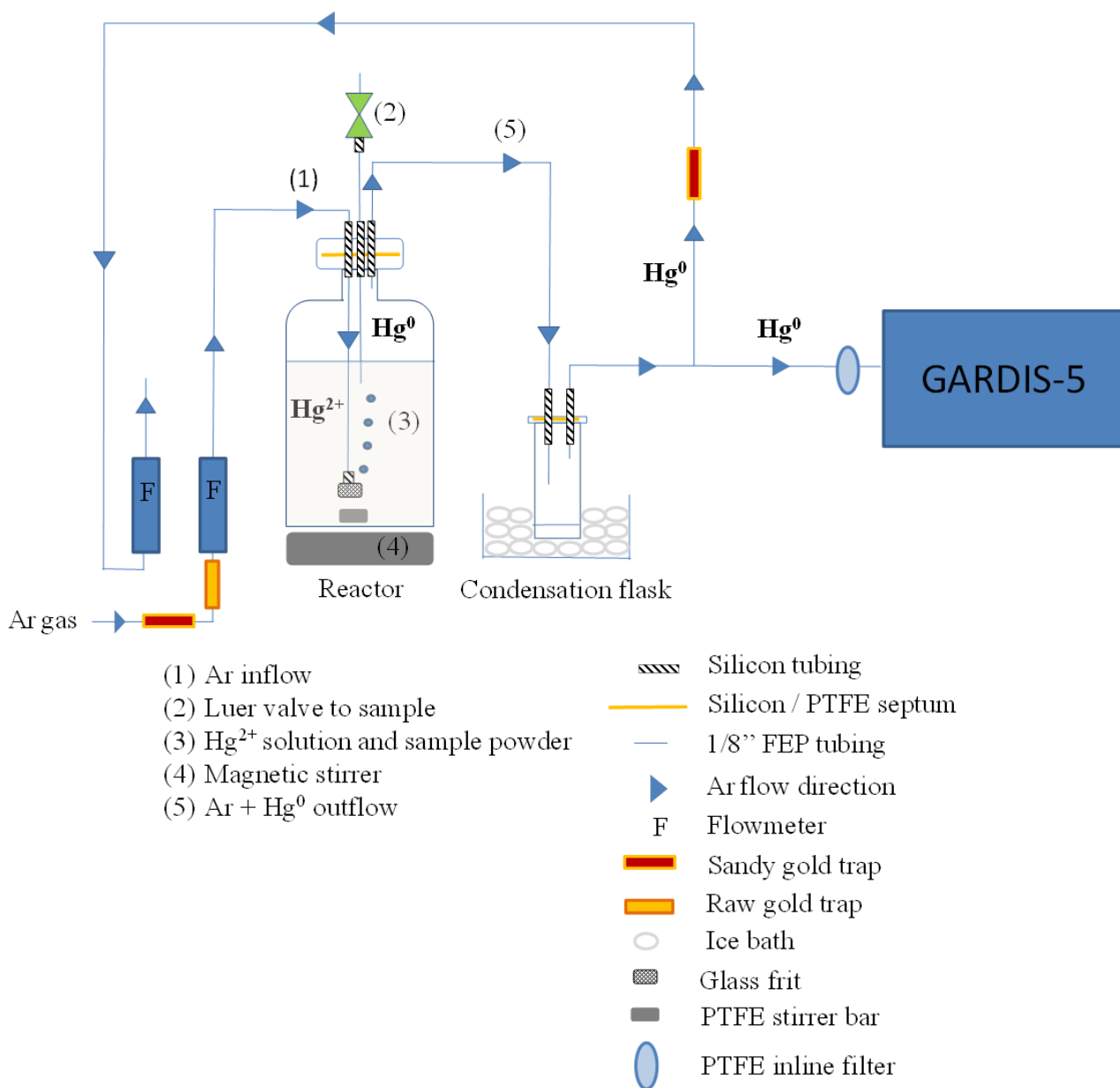


Figure S2: Details of the experimental set-up

3. Result of titration experiment at pH 6 on M/ZVI

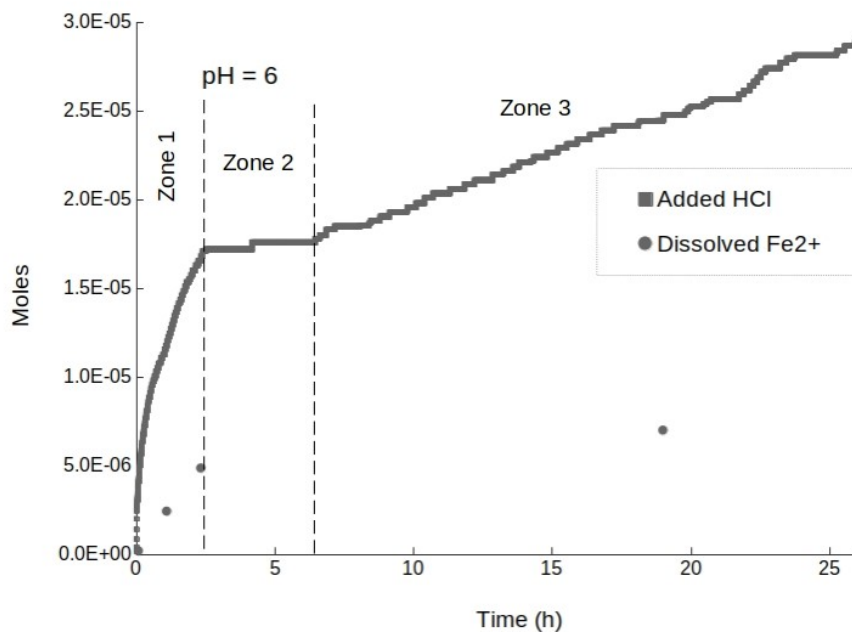


Figure S3: pH metric titration and iron release from the magnetite product at pH 6 using 0.01 M HCl.

4. Calibration of the elemental Hg analyzer (Gardis-5)

Gardis-5[®] was calibrated the same day of each experiment by injecting Hg saturated vapor with a 0-25 μL syringe. The quantity of absolute Hg^0 injected (vapor pressure) was corrected according to ambient temperature and ranged from 2 pg to 557 pg (0.2 μL to 19 μL). Precision was tested by repeating ten times the injection of three volumes of Hg^0 (0.2 μL , 4.8 μL and 15 μL) scanning in that way, the whole calibration range. Linear correlation coefficients in the Gardis calibration were better than 0.99 and precision gave RSD at 12 %, 5 % and 4 % respectively for 0.2 μL , 4.8 μL and 15 μL of injected Hg^0 .

Hg calibrations in the CV-AFS were performed with a daily prepared 50 $\text{ng}\cdot\text{L}^{-1}$ Hg standard solution (NIST certified reference solution). Accuracy was obtained by a double calibration using a 100 $\text{ng}\cdot\text{L}^{-1}$ Hg standard prepared from an HgCl_2 reagent. Precision was obtained by analyzing the same NIST standard solution on a maximum of ten samples for each sequence of analysis. Linear correlation coefficients in the CV-AFS were always better than 0.997. The recovery calculated as the ratio between the calibration slopes obtained with HgCl_2 standards and with the NIST standards,

respectively, varied between 80 and 112 % with a mean value at 95 % (RSD 12 %, N=7). Precision gave a mean value better than 2 % (N= 53).

5. Blank experiments

A series of 5 blank experiments has been carried out to ensure that the Hg^0 production events produced in the presence of the M/ZVI can be attributed to the effect of this composite powder.

In the first blank experiment (Blank-1), the gas analyzed with elemental Hg analyzer was bubbling in a solution containing 25 ng.L^{-1} of Hg^{2+} in 300 mL of ultra-pure water (Fig. S4A) using the set-up described hereabove. A long event Hg^0 production event was encountered with an amplitude which was however close or below the detection limit of the elemental Hg gas analyzer.

The second blank experiment (Blank-2, Fig. S4B) was run with a 10^{-3} M solution of sodium azide (NaN_3). Hg^0 was measured while the pH was varied from 8.1 to 4.3 by HNO_3 addition. Blank 2 was carried out due to the NaN_3 potential to reduce aqueous Hg^{2+} through the $2 \text{ N}_3^- = 3 \text{ N}_2 + 2 \text{ e}^-$ oxidation half-cell reaction ($E^0 = 3.09 \text{ V}$). It shows (Fig. S4B) that Hg reduction, if any, is sufficiently slow at the experiment timescale (20 h) to produce no significant Hg^0 signal. This observation is consistent with the result from Hendrix *et al.* (2019) who showed that the reduction of aqueous Hg^{2+} by NaN_3 is only significant for experiments lasting several days.

For Blank-3, 12.3 mg of M/ZVI was introduced in 300 mL of ultra-pure water without NaN_3 in order to make sure that the powder sample was no source of Hg^0 . This assumption was confirmed by the Blank-3 data (see Fig. 3E of the manuscript) with an Hg^0 which levels 2 pg at most above the baseline determined on pure water.

Similar experiments (Blank-4) was performed using single-phase ZVI (10.4 mg) corresponding to commercial Fe^0 (Alfa Aesar – 00737, $\geq 99\%$), since this starting material has been used in some of the Hg^0 monitoring experiments (Table 1). Again, the Hg^0 signal barely exceeded 1-2 pg above baseline (Fig S4C).

Finally, a last blank (Blank-5, Fig. S4D) was carried out to test the effect of dissolved iron on aqueous Hg^{2+} reduction. ZVI (11.6 mg) was first fully dissolved at a pH of around 2.2 reached using HNO_3 2 % (Optima™, $\text{Hg} < 50 \text{ pg g}^{-1}$). A preliminary test measuring aqueous Fe^{2+} , showed that ZVI quickly dissolves at this pH. Then, pH was increased to 4.1 by NaOH addition which produced a small Hg^0 peak which shows that the NaOH solution (NaOH 2 % obtained by dissolution of Normapur pellets in a solution that was degassed 1h under Ar) contains Hg impurity. HgCl_2 solution was added in order to reach 25 ng.L^{-1} . pH was increased step-wise by addition of NaOH until

a pH 9.1 (Fig. S4D). At each pH step a tiny Hg^0 peak (< 10 pg) is encountered associated with impurity supplied by the NaOH addition. No major Hg^0 event is observed in the whole pH range indicating that Fe^{2+} does not rapidly reduce Hg^{2+} in our experiments. This is consistent with the rate law produced by Amirbahman *et al.* (2013) for homogeneous reduction by aqueous iron considering the low $[\text{Fe}^{2+}]$ recovered in Blank 5 (below detection) which reflects progressive oxidation of aqueous iron in our set-up.

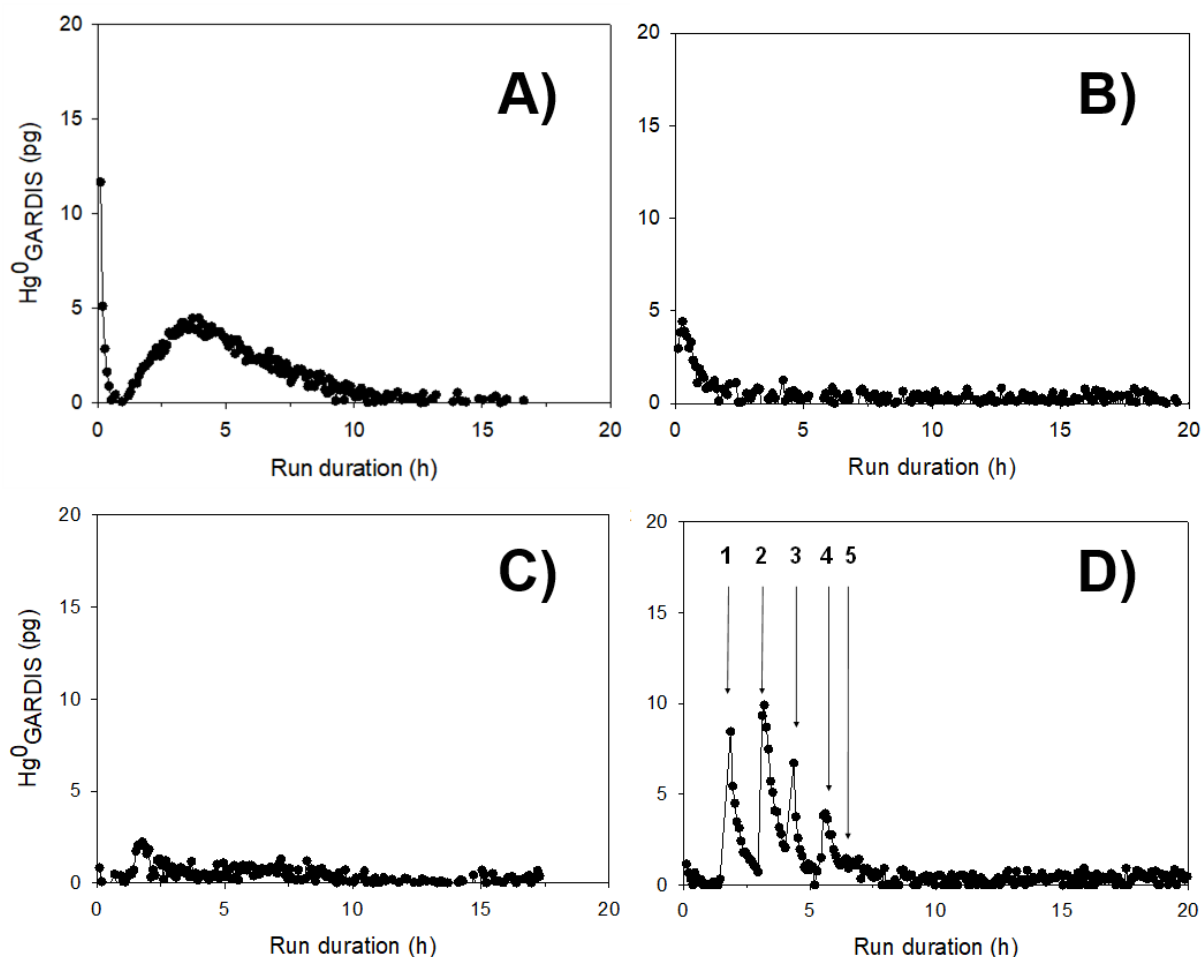


Figure S4: Time-resolved Hg^0 data for the blank experiments. **A)** Blank 1 (25 ng.L^{-1} of Hg^{2+}); **B)** Blank-2 (25 ng.L^{-1} of Hg^{2+} with 1 mM NaN_3), the pH was varied from 8.1 to 4.3 using HNO_3 ; **C)** Blank-4 with 10.4 mg ZVI and no aqueous Hg^{2+} . pH varied from 3.7 to 6.4 upon ZVI dissolution, **D)** Blank-5 (11.6 mg ZVI with 25 ng.L^{-1} of Hg^{2+}). The ZVI was first added at pH 2.2 for complete dissolution. NaOH was added to reach pH 4.1, this produced a tiny Hg^0 peak (1) related to the Hg contained in NaOH as impurity. Then, aqueous Hg was added which produced another tiny Hg^0 peak (2) as in every experiment. NaOH was added again to reach pH 5.9 (3), 8.2 (4) and 9.1 (5). No major Hg^0 production event was encountered. It must be noted that Blank-3 (12.3 mg of M/ZVI) without aqueous Hg^{2+} is not reproduced here since it is already displayed on Fig. 3E.

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