Characterization of the submarine disposal of a Bayer effluent (Gardanne alumina plant, southern France): I. Size distribution, chemical composition and settling rate of particles forming at the outfall

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ABSTRACT

The submarine discharge of the high pH clarified Bayer effluent of the Gardanne alumina plant (Marseille region, France) leads to the formation of concretions at the outfall 324 meters underwater and to a plume of white particles. Calibration of turbidity using effluent/seawater mixing experiments and in situ measurements shows that 1 turbidity unit (NTU) represents about 4.7 mg L^{-1} of suspended particles, allowing to trace the effluent plume in the mixing zone. The bulk chemical composition of the concretions has been determined by SF-ICP-MS. Mg and Al are the major elements measured in concretions with concentrations of a few hundred mg g^{-1} . Ca and S are also found at concentrations in the range of mg g^{-1} . Among the measured trace elements there is a specific interest in As and V because of environmental concerns pointed out by regulation authorities. Their concentrations are of tens to thousands $\mu\text{g g}^{-1}$, respectively. The concentrations of the following elements are in the range of a few hundreds $\mu\text{g g}^{-1}$: Si, V, K, Sr, P, As, B, Mo, Fe, Ti, Cu, Zn, Sn. The concentrations of the other elements are below $1 \mu\text{g g}^{-1}$ down to a few ng g^{-1} : Rb, U, Ba, Cr, Ni, Co, Sb, Mn, Ag, Cd, Pb, Hg, Th. In order to constrain the dispersion of particles in the environment and to understand how chemical elements can be scavenged from or released to seawater, the size distribution of particles composing the concretions has been measured by settling rate experiments and, for each size class of particles, their chemical composition has been determined. For example, As and V are mainly associated to particles with mean diameters between 15.6 and 63 μm and settling rates around 96 m d^{-1} . Overall, all the main elements (Mg, Al, Ca, S) composing concretions are associated to this size class of particles which represents 53 to 60 % of the total concretion mass.

KEYWORDS: Bayer effluent, trace metals, settling rate, size distribution, Gardanne alumina plant, Cassidaigne Canyon, Mediterranean Sea.

1. Introduction

The alumina production plant located in Gardanne (about 30 km North of Marseille in Southern France) was created more than 120 years ago. It is the place where the Bayer process was first implemented in 1893 at an industrial scale. It is nowadays operated by the Alteo Company, which is today one of the first world producers of specialty aluminas. Specialty (or chemical-grade) alumina is dedicated to technological uses at the difference with metallurgical (or smelter-grade) alumina mainly used to produce aluminum by electrolysis. The Bayer process is based on the dissolution of the ore (bauxites) in NaOH solutions at about 250°C and on the precipitation of aluminum hydroxides separated from impurities by decantation and filtration. Al-hydroxides are precipitated with no addition of chemicals (that for example would alter the pH), but by changing the temperature to lower their solubilities and favour nucleation and growth. Oxalate produced during the alkaline degradation of the organic matter contained in bauxites is removed from solution by addition of lime that leads to the precipitation of calcium oxalate. Flocculating agents such as starch may be added in the decanters to increase the settling rate of the particles (Hill and Sehnke, 2006). This industrial process generates a residue generally called "red mud", a slurry also named Bayer residue or Bayer precipitate. One also finds the ambiguous denomination Bayer liquor that can be used to designate either a slurry or a clarified effluent (the liquid part of the red muds). The production of one ton of alumina generates between 1 and 1.5 tons of red muds (Hill and Sehnke, 2006).

From 1967 to the end of 2015, the Gardanne alumina plant has disposed its residues (red muds) in the Mediterranean Sea through a 55 km-long pipe, 7 km of which being under water. The outfall of this pipe is at a depth of 324 m at the top of the Cassidaigne Canyon which cuts the continental shelf off the coast of the Calanques National Park (Figure 1). New regulations in force since January 1, 2016 do not allow any longer the disposal at sea of a

71 slurry, but only that of a high pH (12.5) -high metals content clarified liquid effluent obtained
72 by filtration of the Bayer residue (Bru et al., 2014). The solid part of the waste is now stored
73 in on-land tailing ponds at the Mangegarri site close to the plant. The authorization for these
74 new operational conditions has been in place since 2016 and will expire in 2021. During this
75 5-year authorization period the company is committed to studying the environmental aspects
76 of the effluent disposal at sea. It is also committed to proposing alternative solutions to the
77 present Bayer process that would minimize, and ultimately stop the effluent disposal. The
78 long-term concern of the environmental impacts of this disposal (Dauvin, 2010) had been
79 enhanced after the Ajka (Hungary) red mud spill in 2010 (Mayes et al., 2016). Furthermore, in
80 the case of the Gardanne plant regulation authorities have pointed out particular marine
81 environmental concerns such as the formation of concretions with an important plume of
82 white suspended particles when the Bayer effluent mixes with seawater (Figure 2). According
83 to previous studies on red mud neutralization using seawater (Hanahan, 2004; Palmer et al.,
84 2009), such concretions are made up of hydrotalcite, an Mg-Al Double Layered Hydroxide
85 (Mills et al., 2012). Because of the high capacity of hydrotalcite to scavenge metals from the
86 solution (Cavani et al., 1991), concretions and particles that would form at sea in the
87 Cassidaigne Canyon may play a major role as a sink collection point for metals, or on the
88 contrary in releasing metals to the coastal zone of the Calanques National Park.

89 In this context, the aims of the present study were (1) to collect concretions and
90 suspended particles formed at the outfall of the effluent at sea for the first time, (2) to
91 determine their chemical composition with a specific focus on trace metals, and (3) to
92 measure their settling rate and determine the distribution of chemical elements as a function
93 of particle size. The chemical composition of the source effluent and the mineralogical
94 composition of the concretions are reported in a companion paper (Monnin et al., submitted).
95 This study was part of a broader survey aiming at determining the impact of the discharge of

the Bayer effluent of the Gardanne plant in the Mediterranean Sea, as requested by the French State. Results from the present work will serve as the basis for further studies on the behaviour of trace metals in the context of concretions stability field destabilization due to particle dispersion in seawater or to the effluent discharge suppression or composition changes as it is planned in 2021. Data presented here are the first of their kind and very relevant in the need for a detailed characterization and understanding of industrial waste disposals at sea as well as for an accurate assessment of their consequences (Morello et al., 2016; Ramirez-Llodra et al., 2015).

2. Material and methods

The Bayer effluent of the Gardanne alumina plant is discharged into the sea at a rate of around $270 \text{ m}^3 \text{ h}^{-1}$. The discharge leads to the formation of concretions at the submarine pipe outfall and to a plume of white suspended particles (Figure 2). Two sampling cruises took place on August 24, 2016 and from December 6th to 8th, 2016 on board the *RV Janus* (COMEX company) using the ROV Super Achille (also from the COMEX company). These cruises targeted the zone of the effluent discharge a few kilometres offshore. The effluent plume was observed up to 100 m above the outfall. These cruises allowed to collect for the first time concretions and particles created by the residue discharge.

a) Measurements in samples collected in the effluent plume

Water samples were collected from December 6th to 8th 2016 within the plume and then processed on board. The ROV was equipped with a clean Teflon seawater sampling system. Water samples were taken at 5 depths between 310 and 324 m directly above the outfall of the effluent. An aliquot of about 330 mL of these water samples was filtered on $0.22 \mu\text{m}$ Durapore® PVDF filters and another one (about 100 ml) on $0.7 \mu\text{m}$ Whatman® GF/F

glass filters. These filters were dried at 65°C and weighted before and after filtering to determine the mass of particles.

The turbidity of the water samples was measured on board using a Seapoint turbidimeter (Seapoint Sensors Inc., Exeter, USA) installed on a RBR-MAESTRO probe (RBR Ltd, Ottawa, Canada). Turbidity is expressed in NTU (Nephelometric Turbidity Unit). The turbidimeter has been calibrated using data collected during the measurements in the lab of the particle size distribution and their settling rate (see below).

b) Effluent/seawater mixing experiments in the laboratory

The goal of these experiments was to reproduce in the laboratory the conditions of the underwater effluent/seawater mixing. The source effluent used for the experiments was provided by the Gardanne plant. It was collected during the same period as the effluent plume sampling at sea, i.e. every day at 4 pm between December 4th and 9th, 2016. The variation in the effluent composition is negligible during this sampling period (i.e. about a week, see the companion paper Monnin et al., submitted). For the sake of the laboratory experiments, an averaged effluent was obtained by mixing the effluent samples collected at these various dates.

The seawater used for the experiments was sampled at a depth of 50 m in the Mediterranean Sea in the vicinity of the Cassidaigne Canyon but away from the zone of the effluent discharge. Seawater and effluent aliquots were mixed by volume using five different effluent/seawater ratios: 1/5, 1/10, 1/20, 1/200 and 1/2000. Turbidity was measured before filtration using the same Seapoint turbidimeter as described above. The mixture was then filtered on pre-weighted 0.22 µm Durapore® PVDF filters. Filters were dried at 65°C and weighted to determine the mass of formed particles.

c) Submarine concretions

Concretions were collected on August 24 2016 (*RV Janus II*, COMEX) at the direct outfall of the effluent. Because concretions are very crumbly, a sampling system especially designed by the COMEX company was installed on the ROV next to the monitoring devices. All previous attempts to sample concretions by using direct ROV collection (manipulator arm) were unsuccessful. Briefly, the sampling system designed by COMEX is a cylindrical structure that can be reversed allowing to smoothly collect the concretions avoiding any shaking or brutal movement.

Concretions were sampled at three locations in the close area of the outfall, respectively named H1, H2 and H3. H1 was not venting at the time of the cruise (Figure 3A) in contrast to H2 and H3 as revealed by the presence of a white plume of particles above the concretion massif (Figures 2 and 3C). Concretions are composed of a soft middle white core crossed by orange veins, and an external crumbly crust. H1 was subsampled in 2 cm slices from the core to the external crust (Figure 3B). H2 corresponds to a fragment of the external crust. H3 was subsampled in the core and in the orange veins of the concretion (Figure 3D). All samples were then freeze-dried and kept at 4°C until analyses. On average the water content of the concretions is about 80%. We sorted the samples into three groups (Table 1): samples from the core (group 1), group 2 represents intermediate samples between the core and the external crust (group 2) and groups 3 is the samples taken in the external crust. The mineralogical composition of these concretions is given in a companion paper (Monnin et al., submitted). Briefly, results of this paper showed that H1, H2 and H3 concretions are mainly dominated by hydrotalcite, with white core samples containing pure hydrotalcite and samples from other slices containing assemblage of minerals (hydrotalcite plus calcium carbonate or brucite).

d) Measurement of the settling rate and size distribution of particles

Due to their high friability particles collected in the effluent plume could not be used for the settling rate and size distribution measurements. As these particles form in the concretions before being transferred in seawater through the effluent plume, subsamples taken from the core of concretions have thus been considered analogous to the white particles in the effluent plume. Hence subsamples H1 and H3 “soft core” samples (group 1; Table 1) were used in the experiments.

We followed the same experimental procedure as reported in Oursel et al. (2014). Briefly, the experimental device was composed of a vertical Plexiglas tube (1m long and 10 cm diameter), open at the top and equipped with a valve on the bottom to collect water samples. The tube was filled with 7.5 L of seawater sampled at a depth of 50 m in the area of the Cassidaigne Canyon away from the influence of the discharge. Experiments were performed with 1.3 g and 2.3 g of the freeze-dried concretion samples H1 and H3, respectively. Particles were injected at the top of the vertical tube. Water samples have been collected at the bottom 14 times in two weeks. The first sample was taken 2 minutes after the particle injection and the last one after 15.5 days of experiment, in order to cover a large range of settling rates and particle diameters. The 14 samples were immediately filtered (150 to 350 mL) after collection on pre-weighted 0.22 μm Nucleopore PC filters and 0.7 μm Whatman® GF/F glass filters, dried at 65°C and weighted to determine the mass of particles. Nucleopore PC and GF/F filters have been used for trace metal and Hg analyses, respectively.

Measured settling velocities and particle diameters were then grouped in 4 main size classes of particles based on the Udden-Wentworth sediment grain size scale, according to Leeder (1982) and Bainbridge et al. (2012). The recovery of the injected particles was 93% for H1 and 98% for H3 by weight. This shows that particles did not significantly dissolve during the time of the experiment.

e) Chemical analyses

We dissolved H1, H2 and H3 concretion samples and H1 and H3 “soft core” size classes filters (from settling rate experiments) in a mixture of two acids (HCl/ HNO₃; all Suprapur grade). The solutions were then analyzed for major and trace elements using a Sector Field Inductively Coupled Plasma Mass Spectrometer (SF-ICP-MS; ELEMENT XR, ThermoElement). The instrument was calibrated using standard solutions, and we used an external calibration method with In as an internal standard. The efficiency of the dissolution procedure and the quality of the SF-ICP-MS measurements were controlled by the determination of element concentrations on Certified Reference Materials (MESS-4, SLRS-5, SLEW-3 and CASS-5). Particulate Hg was analyzed by cold vapor atomic absorption spectrometry (CV-AAS, LECO AMA-254).

3. Results and discussion

As revealed by ROV images of the effluent outfall at sea the pipe is nowadays covered with historical red muds (i.e. disposed before January 2015) and debris of concretions (Figure 2). After passing through this cover the effluent mixes with seawater and forms concretions and a plume of white particles. The concretions may form chimneys 3 to 4 m high, surrounded by debris of these chimneys and covering an area of about 170 m². These chimneys look like pinnacles observed at the Lost City (mid-Atlantic ocean) or Prony (New Caledonia) that are natural hyperalkaline hydrothermal vents (Kelley et al., 2001; Monnin et al., 2014). ROV observations in the Cassidaigne Canyon show that particles from the effluent plume extend up to 100 m above the outfall (i.e. to a depth of about 200 meters below sea level).

a) Particles concentration, size distribution and settling rate

The concentration of particles in the clarified liquid effluent produced by the Gardanne plant is around 25 mg L^{-1} . The suspended particle concentration measured in the water column within the effluent plume at sea ranges from 20 to 274 mg L^{-1} (Figure 4). The relation between the concentration of suspended particles and turbidity has been established by the effluent/seawater mixing experiments and is similar to the one obtained from measurements of the samples collected at sea by the ROV. The two datasets display a unique trend with a slope of 4.7, which indicates that 1 NTU corresponds to 4.7 mg L^{-1} of suspended particles. An estimate of the mixing ratios of the samples collected at sea can be obtained from the measured turbidity and from the curve calibrated by the laboratory data. The turbidity of these samples is between 4.9 and 64.6 NTU. As such, samples collected at sea would correspond to mixing ratios from 1/8 at the direct outfall to 1/190 10 m above the outfall.

The distribution of particles as a function of their settling rate is given in Figure 5. H1 and H3 “soft core” samples present a similar distribution of particle sizes. As reported above, settling velocities and particle diameters were then grouped in the 4 main size classes of particles according to the Udden-Wentworth scale (Table 2). Settling rate values range from less than 1 m d^{-1} (fine fraction) to more than 500 m d^{-1} (sand). The larger fraction of the particles lies in the “coarse silt” category, which corresponds to particle diameters between 15 and $63 \mu\text{m}$ and a settling rate of about 1 mm s^{-1} , i.e. 86 m d^{-1} . The second largest fraction, 22 and 23 % of the sample weight respectively, corresponds to particles whose settling rate is about 500 m d^{-1} , and an estimated diameter larger than $63 \mu\text{m}$ (sand). The remaining fractions (fine silt and fine fraction) correspond to particles which settling rate is lower than 10 m d^{-1} . Overall, the main particle fractions of concretions have relatively high settling rates. Compared to natural marine particles, these would correspond to particles generally called fast-sinking particles. The major part of the particles formed by the mixing of the effluent and

seawater will thus rapidly sink and in the vicinity of the outfall, at the difference with the slurry (red muds) that has been discharged at the top of the Cassidaigne Canyon until 2015 and expanded far away from the outfall by gravity flow.

b) Chemical composition of the concretions

The major elements of the concretions are Mg, Al, Ca and S (Figure 6A). Concentrations range from 316 to 626 mg g⁻¹ for Mg, 84 to 340 mg g⁻¹ for Al, 7.6 to 52.1 mg g⁻¹ for Ca and 2.2 to 12.8 mg g⁻¹ for S (Table 1). The average concentrations are reported in Figure 6B-C for the three groups of concretions. Among the minor and trace elements, As and Co present trends similar to that for Al, with lower concentrations in the core compared to the crustal layer of the concretion (Figure 7A-A'). Higher V concentrations also appear associated with the central/intermediate part of the concretion while Fe is mainly concentrated in the external parts (Figure 7B-B'). Similarly to Fe, Mo and Ti (Figure 7C-C') and Pb and Cd (Figure 7D-D') are also enriched in the crust, as Mg and Ca. Other elements presenting the same trend as Al are Cu, Ag, Sn, Hg, Si, P and Rb, while B, Th, Sr, K, U, Ba, Cr, Mn, Ni and Zn present the same trend as Ca and Mg (not shown). Minimum, maximum and average values for all the elements analysed are reported in Table 3 next to upper and lower continental crust values (Wedepohl, 1991) which are generally used to trace material from continental origin. On average Mg, As and Mo concentrations in the concretions are 23-25 times higher than continental crust values. V and S are 12 times higher and Al is 3 times higher. Ca (group 3) and Cd concentrations are of the same order as continental crust values. All the other elements present on average concentrations from 10 to 10³ times lower than continental crust values.

As reported above, H1 and H3 “soft core” samples (group 1) can be considered analogous to the white particles found in suspension in the effluent plume at sea. With regards to concentration levels, these are composed on average by: (1) of Mg, Ca, Al and S at

concentrations between a few tens to hundreds of mg g^{-1} , (2) few to ten of mg g^{-1} of V and Si, (3) hundreds of $\mu\text{g g}^{-1}$ of K, Sr, P and As, (4) tens of $\mu\text{g g}^{-1}$ of B, Mo and Fe, (5) few $\mu\text{g g}^{-1}$ of Ti, Cu, Zn and Sn, (6) hundreds of ng g^{-1} of Rb, U, Ba, Cr, Ni, Co, Sb, Mn, and (7) tens of ng g^{-1} of Ag, Cd, Pb, Hg and Th (Table 3) .

The chemical composition of particles of the different size classes was also determined. Figure 8 reports the distribution of the chemical elements between the 4 main size classes of particles, in an order determined by their content in the coarse silt fraction, which is the larger fraction of particles in H1 and H3 (Table 3). 50 to 70 % in weight of Al, Mg, Ca, S, V and As are concentrated in this fraction. In contrast, elements found in lower concentrations are associated to fine silt or sand fractions. Overall, these results outline the importance of for the size of the particles on the transfer of metals in seawater. A recent study on the levels of fish contamination in the Cassidaigne Canyon area has shown that fish would especially be contaminated by Al and to a lesser extent by Ti and V (Bouchoucha et al., 2019). These elements are indeed among the main elements found in the concretions and particles. The direct impact of the actual effluent discharge is not easy to assess because element bioaccumulation in fish is blurred by interaction with biological effects (trophic level and size). The evolution of the historical red mud deposited on the seafloor can also play a role in releasing metals to seawater. A better understanding of the different sources of metals (historical red mud, actual effluent, concretion particles and impacted seawater) and the trophic structure in the Cassidaigne Canyon will provide greater evaluation of the health risk for humans consuming fish from the area.

4. Conclusion

Submarine concretions and white particles plume form when the high pH clarified Bayer effluent of the Gardanne alumina plant mixes with seawater in the Cassidaigne Canyon (NW-Mediterranean Sea). We estimated effluent/seawater mixing ratios of around 1/8 at the direct

outfall to 1/190 10 m above the outfall. We estimated that 1 NTU (turbidity) would represent 4.7 mg L⁻¹ of particles, allowing to trace the effluent plume in the mixing zone. Next to the major elements Mg, Al, Ca and S, As and V are the main trace metals found in the concretions. Concretions are mainly composed by aggregated particles falling in the category of coarse silt, according to the Udden-Wentworth scale, thus corresponding to diameters between 15.6 and 63 µm. When suspended in the water column these particles would settle at a sinking velocity of around 96 m d⁻¹. Particles transferred by the plume will probably rapidly reach the sediment. However, investigating the fate of the particles formed by the discharge of the clarified effluent will also require to take into account the dispersion of the particles at the same time as their dissolution during their transport in the water column. This would allow a better evaluation of the potential impact of the effluent in the coastal zone.

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315 « Transfer of contaminants in the Mediterranean”).

316 Our colleague Cédric Garnier, who had played key roles in the elaboration and
317 advancement of this project has passed away during this work. May he rest in peace.

Figure captions

Figure 1: Location of the effluent outfall at 324 m depth at the top of the Cassidaigne Canyon (south of France; north-western Mediterranean Sea).

Figure 2: View of the outfall of the effluent at sea (ROV images). The mixing between the effluent and seawater leads to the formation of massive concretions, with an important plume of white particles.

Figure 3: Concretions sampled in the Cassidaigne Canyon: (A) column H1 at sea (ROV image), (B) column H1 subsampled in 2 cm slices from the core to the external crust of the concretion, (C) column H2 and particles plume at sea (ROV image) and (D) fragment of column H3 presenting orange veins.

Figure 4: Relationship between the concentration in suspended particles (mg L^{-1}) and turbidity (NTU) using in situ measurements with the ROV and laboratory mixing experiments.

Figure 5: Variation of the percentage of particles for each class as a function of their settling rate and calculated diameter for H1- and H3- “soft core” samples.

Figure 6: Concentrations (log scale) of the major elements (Mg, Al, Ca and S) of concretions in $\mu\text{g g}^{-1}$ (A). Average concentrations (mg g^{-1}) of same elements for the three groups of concretions: (B) Mg and Al and (C) Ca and S. Group 1: core samples, Group 2: intermediate samples and Group 3: crustal samples.

Figure 7: (A-D) Concentrations in Co (ng g^{-1}) and As ($\mu\text{g g}^{-1}$), Fe and V ($\mu\text{g g}^{-1}$), Ti and Mo ($\mu\text{g g}^{-1}$) and Pb and Cd (ng g^{-1}) for all the samples. (A'D') Concentrations of the same elements for the three groups of concretions. Groups: same as reported in Figure 7.

345

346 Figure 8: Element distributions between each of the 4 main size classes of particles, ordered
347 by increasing content of coarse silt (15-63 μm ; settling rate between 2.0×10^{-2} and 3.3×10^{-1}
348 cm s^{-1}), the major fraction of particles composing H1 and H3 soft core concretions.

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Tables

Table 1: Concentrations of the major elements in the concretions: Mg, Al, Ca and S (mg g^{-1}).

On average water content of the concretions is about 80%. Group 1: core samples, Group 2: intermediate samples and Group 3: crustal samples.

Table 2: Characteristics and chemical composition of the 4 main size classes of particles composing H1 and H3 “soft core” concretion samples. Measured settling velocities and particle diameters are grouped in 4 main size classes of particles based on the Udden-Wentworth sediment grain size scale, according to Leeder (1982) and Bainbridge et al. (2012): sand ($> 63 \mu\text{m}$; settling rate $> 3.3 \times 10^{-1} \text{ cm s}^{-1}$), coarse silt ($15\text{-}63 \mu\text{m}$; settling rate between 2.0×10^{-2} and $3.3 \times 10^{-1} \text{ cm s}^{-1}$), fine silt ($3.9\text{-}15 \mu\text{m}$; settling rate between 1.3×10^{-3} and $2.0 \times 10^{-2} \text{ cm s}^{-1}$), and fine fraction ($< 3.9 \mu\text{m}$; settling rate low $< 1.3 \times 10^{-3} \text{ cm s}^{-1}$).

Table 3: Minimum, maximum and average concentrations of all the elements analysed in the concretions, next to UCC and LC reference values (Wedepohl, 1991). UCC: continental crust, LC: lower crust. Elements are ordered by decreasing mean concentrations for group 1 (from mg g^{-1} to ng g^{-1}).

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