

The effect of high power ultrasound on an aqueous suspension of graphite

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Keywords: Graphite sonolysis; Granulometry; Organic matter; Atmospheric pressure chemical ionization (APCI)

Abstract

Ultrasound treatment was used to study the decrease of the granulometry of graphite, due to the cavitation, which allows the erosion by separating grains. At a smaller scale, cavitation bubble implosion tears apart graphite sheets as shown by HRTEM, while HO[•] and H[•] radicals produced from water sonolysis, generate oxidative and reductive reactions on these sheet fragments. Such reactions form smaller species, e.g. dissolved organic matter. The methodology proposed is very sensitive to unambiguously identifying the *in-situ* composition of organic compounds in water. The use of the atmospheric pressure chemical ionization (APCI) Fourier transform mass spectrometry (FTMS) technique minimizes the perturbation of the organic composition and does not require chemical treatment for analysis. The structural features observed in the narrow range ($m/z < 300$) were mainly aromatic compounds (phenol, benzene, toluene, xylene, benzenediazonium...), C₄-C₆ alkenes and C₂-C₁₀ carboxylic acids. Synthesis of small compounds from graphite sonication has never been reported and will probably be helpful to understand the mechanisms involved in high energy radical reactions.

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1. Introduction

Graphite material is a neutron moderator used in some kinds of nuclear reactors (Uranium Natural Graphite Gaz, Advanced Gas Reactor, and High Temperature Reactor). More than 250000 tons of irradiated graphite are stored worldwide awaiting either final storage or a decontamination treatment before potential re-use. A possible route of irradiated graphite recycling is mechanical erosion by means of exposure to ultrasounds in aqueous media, i.e. the graphite comminution as a first treatment step. Many treatments methods were proposed for graphite management including incineration [1] and pulsed current plasma [2]. These investigations mostly concerned the technical and the feasibility aspects and the economical issues were not studied. The present work was focused on studying in detail the chemical and physical effects of ultrasound on graphite. It is too early to estimate the cost of the proposed treatment method because of numerous parameters involved. But the technical effectiveness was the major motivation of our study.

Physical ultrasonic treatment of crystalline materials is known to sensibly decrease granulometry [3]. From a feed monodispersed granulometry, an increase of the size distribution is observed with comminution time, with a shift to the smallest granulometry. Particles with irregular shape surfaces are easier to break than those with a smooth surface. Graphite material used for our experiments has a disc shape with smooth surfaces and is expected to be difficult to decrease its granulometry under the medium grain size.

High pressures and high temperatures generated by cavitation bubbles implosion undergo violent collisions between particles at very high speed. These extreme conditions allow the water dissociation in HO[•] and H[•] radicals [4-8], which are subject to react with the sonolized material or they recombine to form for example H₂O₂. The radical reactions are usually destructive and ultrasonic treatment are very effective in breaking C-C bonds, oxidizing carbon and *in fine* eliminating organic pollutants in wastewater [9,10]. Nevertheless, ultrasound treatment of carbonaceous matter can also have a constructive effect like for the synthesis of fullerene C₆₀ from

benzene [11], the synthesis of carbon nanotubes from (di)chlorobenzene catalysed with ZnCl_2 [12], or also an allotropic transformative effect with the conversion of graphite into diamond [13]. More complex transformations are also available in literature such as milk sonication [14] to create C_6 - C_9 alkenes, benzene, toluene, p-xylene, hexanal and heptanal, or such as sunflower oil sonication [15] to generate mainly limonene and hexanal.

Thus ultrasound treatment on carbonaceous material releases new organic molecules of pyrolytic origin. Moreover, incomplete combustion of rich-carbon materials is well known to release hydrocarbons, aldehydes, ketones, esters... produced by radical reactions including HO^\bullet , R^\bullet , RO^\bullet and ROO^\bullet ($\text{R} = \text{C}_x\text{H}_y$). This phenomenon is widely reviewed in literature in forest fire smokes studies [16]. Most important aromatic compounds formed in this kind of combustion are notably benzene, toluene, ethylbenzene/xylenes (BTEX), phenol, methylphenols, etc. All these Volatile Organic Compounds (VOCs) are recognized to be hazardous atmospheric pollutants that might harm the environment, human health [17] and the flora.

The VOC problematic and origin are natural (forest fires [18]) and domestic (wood fires in fireplaces [19]) but could also be from industrial origin (petrochemistry, chemistry...). But beyond the release in the atmosphere, wood residues from forestry exploitation can be promoted by conversion into liquid oils [20] and biomass can be re-used for fuel and chemistry applications. The increasing interest for hazardous pollutants released in the atmosphere strengthens the interest of this environmentally thoughtful study.

Usual tools to understand the characteristics of organic components are NMR, pyrolysis-GC/MS, IR and thermogravimetry. This kind of analysis may not be generally applicable because it is time consuming, expensive and require considerable operator expertise. Therefore, it would be valuable to develop rapid analytical methods that require only a small sample volume and minimal pretreatment. Mass spectrometry with either electro spray ionization (ESI) or atmospheric pressure chemical ionization (APCI) modes has been proved to be a powerful tool for "environmental type analysis" such as molecular weight distribution of aquatic humic substances [21]. It was recently

reported that this instrumental approach could be helpful to investigate ambers, a fossil resin of organic polymers, from different origin [22]. The main advantage of these instrumental methods is based on the fact that no derivatisation of the functional groups has to be done before analysis since a direct analysis of the water is performed, in contrast for instance to GC/MS. One of the drawbacks could be linked to the presence of salts in solution leading to noisy information on MS signal.

In this paper, the effect of the sonication, and especially the sonication power, on the graphite powder will be discussed based on a material characterization. We will focus on the determination of the resulting neo-formed compounds during graphite sonication. A mechanism will be proposed. In particular, one of the major objectives is to determine accurately the composition of organics as a function of the ultrasonic intensity and to study the kinetics of formation / consumption of these compounds. Only Mass Spectrometry allowed identifying the presence of these organic species as well as their composition.

2. Material and method

2.1. Ultrasonic treatment

Graphite compact was obtained from Areva NP. Two powders were prepared: the first by crushing the compact into a silicon nitride bowl mill (with a Pulverisette from Fritsch), called powder A, and the second by crushing it in a ceramic mortar and then sieved at 630 μm , called powder B. 1 g of powder was used for all experiments. The ultrasound device was a Lixea Formulator D1000 manufactured by Sinaptec. The nominal maximal electric power was 500 W, working at the frequency of 19.7 kHz. Two probe geometries were used: the probe A had a diameter of 25 mm, the probe B had a rectangular section of 10 mm x 55 mm. They are made of the titanium alloy TA6V. A previous blank experiment without graphite showed by inductively coupled plasma-mass spectrometry (ICP-MS) the release of elements from the TA6V (Ti, V, Al) plus Na, K and Cu. Ultrapure water used for experiments was Millipore MilliQ (at 18.2 $\text{M}\Omega\cdot\text{cm}^{-1}$). A volume of 1 L was degassed to remove N_2 , O_2 and carbonates, transferred into the reactor (a thermostated glass beaker of 2 L) and then the solution was saturated with argon by continuous bubbling by means of a polyetheretherketon (PEEK) tube. After 10 min of bubbling, graphite powder was added and ultrasounds were applied at different powers, continuing bubbling. Previous calibration experiments permitted to convert the electric power to the thermal power using the calorimetric method [23]. The intensity is calculated dividing the thermal power by the probe section area. Experiments were carried at intensities of 10, 20 and 30 W/cm^2 and durations were variable but at a constant temperature fixed at 20 $^\circ\text{C}$ with a cryothermostatic bath Huber Ministat (400 W), coupled at a platinum temperature sensor. For some experiments, samples were taken to measure pH, the H_2O_2 formation and the granulometry. Hydrogen peroxide concentrations were analyzed using the Ghormley method [24] by UV-Vis spectrophotometry.

After treatment, a typical odor of organic compounds can be smelt, and the black solution is transferred into a Duran brown flask and stored at 4 °C, awaiting MS analyses.

2.2. *Laser granulometry analyses*

The goal of laser granulometric analyses is to underline the strong macro- and microscopic effect of ultrasound on a powder granulometry and to provide quantitative data on the first step of the graphite desegregation. The experimental conditions were the same as those described above, using the probe B (10 mm x 55 mm) and working at the three intensities mentioned. The raw material was the powder B. For each intensity, three samples were collected at times 25, 50 and 100 min and are kept under moderate shaking for one night before analysis. The laser granulometry device was a Beckman Coulter LS 230, using the liquid method. Samples were diluted in a manner to obtain an obscuration rate between 7 % and 10 %. The optical model was Fraunhofer and each analysis ran 60 s.

The dispersion coefficient ξ is calculated via the equation [3]:

$$\xi = \frac{x_{84} - x_{16}}{2 x_{50}} \quad (1)$$

where x_i denotes particle size at a cumulative value of $i\%$. x_i values are determined by interpolation.

2.3. *HRTEM observations*

High-Resolution Transmission Electronic Microscopy (HRTEM) analyses were performed on a Hitachi H-9000 NAR operating at 300 kV. In samples prepared from the powder A and the probe A, at an ultrasonic intensity of either 20 or 30 W/cm², *ceteris paribus* were observed. A first aliquot was directly taken from the sonolyzed water and disposed on the copper grid; A second aliquot was dried (by natural water evaporation), grinded in an agate mortar with ethanol and then disposed on the copper grid. The objective of these two observations is to see how graphite crystallites break during the cavitation bubble implosion and how are the morphologies of the resulting fragments.

2.4. *Mass spectrometry analyses*

A LTQ XL Orbitrap (Thermo Fisher) mass spectrometer was employed. The samples were prepared using the powder A at 20 W/cm² and then filtered at 0.45 μm. They were introduced by direct infusion into the source with a syringe pump at a flow rate of 3 μL/min. Ultrapure water was used as a sheath solvent at a flow rate of 0.6 mL/min. It was the same ultrapure water as the one used before sonication. The following parameters were set: vaporizer temperature 300°C, capillary temperature 200°C, capillary voltage 25 V. The Corona needle voltage was set at 2.5 kV and the discharge current was 2 μA. The device is equipped with a high resolution Fourier Transform MS analyzer, which allows the accurate real mass determination with an absolute maximal error of -0.0005 m.u. in positive mode and ±0.0004 m.u. in negative mode. This accuracy is enough to determine exactly the molecular formula with atoms ¹H, ¹²C, ¹⁴N and ¹⁶O of which masses are respectively 1.007825, 12.000000, 14.003074 and 15.994915 atomic units.

3. Results and discussion

3.1. Laser granulometry

The technique consisting in decreasing the material granulometry is known as comminution. Exposure of solids to ultrasound can decrease the size of particles as has been found in studies on crystalline materials into water with a probe [3] or on dry blocks with a roller press [25,26]. Granulometric curves are presented in figure 1. The untreated graphite powder ($< 630 \mu\text{m}$) is called 'reference'. The corresponding x_i values are reported on figure 2. The initial dispersion coefficient is equal to 0.96 (using the equation 1). This parameter rapidly decreases to about 0.6 for treatments at 10 and 20 W/cm^2 , and to about 0.7 at 30 W/cm^2 . Its evolution is not really significant despite the evolutions of the overall granulometries.

Regarding figure 1, the two main observations are:

- The more intense is the ultrasonic treatment, the smaller the granulometry is,
- The longer the treatment duration is, the smaller the granulometry is.

In fact, these two parameters (intensity and comminution time) shift the curves towards the left (small granulometries). The shift is more important for large granulometries (right side of the curves) than for small ones (left side), indicating that large particles are easier to break compared to smaller ones with the same energy. This observation is also visible in figure 2: x_{84} values decrease more rapidly than x_{16} values. The great differences between the specimen 'reference' and others also demonstrate the rapid granulometry decrease at the beginning of the treatment. Continuing the treatment during a long time, the granulometry decrease slows down drastically. For all treated samples, several populations seem to be present, larger ones decreasing their number to come closer smaller ones. In the three series, the medium particle size (x_{50}) decreases at 35.35, 29.75 and 22.19 μm for respective intensities of 10, 20 and 30 W/cm^2 after 100 min. To avoid the effect of the intensity, the plot of granulometry versus energy density (figure 2) instead of time is more pertinent. So, we observe that for a same energy density, the particle size is smaller using a high intensity than

a low intensity, except at low energy density between 10 and 20 W/cm². This means that high intensity permits more easily to cross the threshold to break particles. A comminution application of graphite via this method should be more efficient working at high intensity, at least at 30 W/cm².

The laser granulometry technique being in the limit of detection near the micron scale, electronic microscopy is then used to characterize the shape and the morphology of sub-micron particles down to the nanoscale.

3.2. *HRTEM observations*

HRTEM on sonolyzed graphite shows grains presenting several damages. In fact these graphite nanosheets are subjected to tearing in the direction of *a*. These nanosheets are size-equivalent to those recently obtained by Li et al. [27] from carbon black sonication. We can observe the crystallites before (Figures 3A, 3B) and after ultrasound treatment (Figures 3C-3F), showing sheets turn-around-ending (indicated by arrows in Figure 3C), loop-endings (Figure 3E) and curve-endings (Figure 3F). These 'defects' have dimensions between 1 nm (loops) and 2 nm (turn-around). These photographs are not isolated cases and suggest the great damages encountered by graphite during sonolysis, which was not observed on natural untreated graphite. The turn-around-ending are similar to the carbon nanotubes extremity. Figure 3D shows very thin nanosheets (about two or three graphite sheets) with a thickness less than 1 nm, and crossed together. These sheets are difficult to see due to the preferential orientation; only sheets perpendicular to the electron beam can be seen.

All these 'defects' can be generated by the cavitation bubble implosion near the graphite surface. During the tearing of the crystallite by the high pressure, the remaining graphite sheets (at the extremity) are modified. The material forms faggot and its extremity is curved (like in figure 3F). If the free sheet is long enough, the formation of loops is possible (figure 3E). It is obvious that during a tearing, free little fragments are also generated. These fragments, via their very sharp size,

have a greater reactivity with radicals to form organic matter. Some amorphous organic matter was observed too, which rapidly huddled up under the beam.

After studying the solid phase by laser granulometry and TEM, the liquid phase analysis will give us new information at smaller scale.

3.3. *pH and H₂O₂ tendencies*

Evolutions of pH and H₂O₂ formation are plotted in figure 4, for an intensity of 20 W/cm². For intensities of 10 and 30 W/cm², pH and H₂O₂ tendencies are similar; nevertheless at 20 W/cm² we observe the biggest differences with and without graphite.

Concerning the pH, with or without graphite, the two experiments show the same tendency with a rapid decrease the first hour of ultrasonic treatment to reach a pH around 4. After 80 min, the two curves are the same, indicating that the pH evolution is not attributed to the presence of graphite. Moreover, pH curves for intensities at 10 and 30 W/cm² are much more similar all during the treatment. The explanation of the pH drop is the oxidation of traces of atmospheric nitrogen with oxygen via sonolysis and the production of HNO₂ and HNO₃, as it is well known [28-29]. In addition, nitrate ion in graphite solution was detected by APCI mass spectrometry (see section 3.4) and ion chromatography where concentrations as high as 10 mg/L were measured. This phenomenon has also been reported by Abdelouas et al. [30] who studied water γ radiolysis. Hypothetic reactions between the carbon matter (here the graphite) and hydrogen (here H⁺ and H[•]) do not change the pH, so we can not speculate on these reactions on the basis of the change in pH.

Concerning the H₂O₂ formations (via $2 \text{HO}^{\bullet} \rightarrow \text{H}_2\text{O}_2$), the blank experiment indicates a zero-order kinetic, with a constant rate formation of 1.58 $\mu\text{mol}/\text{min}$, corresponding to a yield of $1.2 \cdot 10^{-10} \text{ mol}/\text{J}$. It is interesting to note, that this is about 500 times lower than the radiolytic yield for H₂O₂ production from alpha radiation [31]. In presence of graphite, the H₂O₂ formation is lower from the beginning of the treatment on (0.85 $\mu\text{mol}/\text{min}$) and slows further down all during the ultrasonic treatment probably due to the increase of specific surface. By difference, the total

consumed H_2O_2 after 300 min can be estimated at 338 μmol . H_2O_2 is known to react with graphite [32] but the kinetic is slow. In fact, the loss in H_2O_2 can probably better be explained by the HO^\bullet consumption, which is expected to be extremely fast. The HO^\bullet consumption corresponds to about 0.68 mmol, which have reacted with carbon.

The next step in the scale drop is to measure smaller molecules in the water via mass spectrometry.

3.4. *APCI results*

For all these experiments, no matrix was used nor was chemical treatment required to avoid disturbances of organic molecules compared to other ionization modes. APCI can give a general view of the species exhibiting the highest proton affinities. Positive ionization mode APCI+ provides information mainly on protonated hydrocarbons and alcohols (see supplementary materials) whereas negative ionization mode APCI- provides information on deprotonated carboxylic acids (see supplementary materials). Table 1 summarized the main identified compounds which carbon atoms were reduced by H^\bullet radicals. Table 2 indicates the presence of compounds from which carbon atoms were oxidized by HO^\bullet radicals.

Even if APCI is one of the softest ionization mode, it can lead to some fragmentation of molecules, like small aliphatic moieties such as C_4H_3^+ , C_4H_5^+ , C_4H_7^+ , C_4H_9^+ , C_5H_5^+ , C_5H_7^+ , C_5H_9^+ and $\text{C}_5\text{H}_{11}^+$. However, the major detected fragment corresponds to the phenyl group which comes from phenol (water loss), as seen in Figure 5. Phenol is widely detected due to its low volatility. Benzene, toluene, xylenes (BTX) and other alkylbenzenes are weakly detected but hydrogenated equivalents one, two and/or three times are also presents and confirms the mechanism of hydrogenation by H^\bullet radicals produced during water sonolysis or by H_2 (via $2 \text{H}^\bullet \rightarrow \text{H}_2$) catalyzed by the platinum sensor. Hydrogenated equivalents of phenol are also present. Some nitrogen-containing compounds (like butenamine, benzenediazonium, amino compounds) were also detected due to the nitrogen sorption on graphite before sonication, or coming from the silicon nitride bowl during grinding. Silicon is

thus present via Si_3N_4 and/or via the glass reactor, giving trimethylsilyle and silicic acid. Nitrated compounds are then oxidized during sonication and are sensitively detected in APCI-. The nitrogen is coming from the atmosphere. Then it is oxidized into nitrate, which is found in greater yield than organic compounds.

Some peaks are not identified and come from compounds with heteroatoms other than H, C, N and O, or come from identified impurities like bromide (Br^- and Br_2) or sulfur. Thus, sulfur reacted *in situ* with neo-formed species, mainly with aromatic compounds (benzene) to form for example sulfobenzene, the strongest detected compound. Adding relative intensities of all compounds with or issued from an aromatic cycle in APCI+, these compounds represent around three quarters of the detected molecules in this range of m/z with an ionic current of $5.6 \cdot 10^6$ (a.u) in intensity.

The formation of metal complexes coming from the titanium alloy (e.g. Ti, V, Al: $\text{Al}(\text{NO}_2)_2(\text{NH}_3)_2^+$) could be also suggested.

Oxidized compounds are mainly monocarboxylic acids and/or alcohols (acetic, propionic, glycolic, butyric, lactic, valeric, caproic, benzoic, caprylic, pelargonic and capric acids or ramified equivalents, and glycerol) and carbonate which is the last species in the oxidation chain of carbon. We easily notice that these compounds like formic acid and some diacids are commonly found in the oxidative degradation chains by HO^\bullet radicals in the Fenton cycle [33-38]. In the present work, only monoacids are detected, maybe due to the CO_2 loss in diacids (oxalic \rightarrow formic; malonic \rightarrow acetic; succinic \rightarrow propionic; glutaric \rightarrow butyric; adipic \rightarrow valeric; etc...). Formic acid is out of the detectable m/z range with $[\text{M-H}]^- = 45$. Nevertheless, monoacids and dimer are too weakly detected to observe the CO_2 loss. Concerning the carbonate detection, we can notice that the continuous bubbling of argon during sonication eliminates the neo-formed CO_2 , thus suggesting the low carbonate concentration.

The presence of some impurities like sulfur generates some exotic compounds which formation is more difficult to explain. Nevertheless, if impurities are present, the corresponding groups (NH₂, SO₂...) attach to aromatic cycles.

The high resolution and high sensitivity of FTMS APCI emphasize the presence of aromatic compounds which cycles are issued from the graphite structure. These precursor compounds (BTX) play the role of the genesis for all reductive and oxidative reactions with radicals. Intermediate molecules (partially saturated cycles) are thus present, showing the hydrogenation and hydroxylation mechanisms of the carbon chains. Finally, more oxidized and smaller molecules (acids) are detected due to the rupture of C-C bonds.

In summary, based on treated graphite granulometry, HRTEM investigations, and mass spectrometry measurements, we propose the following mechanism for graphite degradation by ultrasonic waves in water (Figure 6).

4. Conclusions

It was evidenced that conversion of graphite into organic matter is possible via ultrasound treatment. We showed via a down-scaling development (laser granulometry and TEM for the solid phase, pH, UV-Vis and FTMS for the liquid phase) the following results:

- Laser granulometry showed a rapid decrease of the graphite granulometry during ultrasound treatment since the earlier minutes. Particles size decreases with time and intensity of treatment. For a same energy density, using a higher intensity favors the granulometry decrease.
- TEM observations showed the graphite morphology, which is greatly damaged and presents unusual shapes. The end of crystallites indicates tearing during cavitation bubbles implosion, suggesting the release of smaller pieces in the medium. These fragments (free or nearly free graphite sheets) are subject to react easily with radicals created during water sonolysis.
- The evolutions of the hydrogen peroxide formation indicated a consumption of radicals HO^\bullet (0.68 mmol) by graphite.
- The FTMS APCI method was efficient enough to characterize the neo-formed organic matter despite that their quantity is low due to evaporation and bubbling. The main organic compounds detected by this method were the aromatic cycle. BTX and phenol can be considered as the main precursors, at the genesis of the disintegration chain.

These new results open a novel field of research to prevent VOC releases or eventually to synthesize them at a larger scale. A best knowledge of the encountered phenomena is necessary and other experiments are in progress:

- to characterize the organic matter via the static headspace method in SPME coupled with a GC/MS system,
- to study their kinetics of formation/destruction,
- to determine the role of the dissolved gas (with hydrogen bubbling, and without bubbling).

Acknowledgements

The authors wish to acknowledge Fabrice Monteau from Laberca laboratory, Nantes, for his precious help during mass spectrometry analyses, Éric Gautron from IMN, Nantes, for his high quality perusal and comments on the TEM observations, and Stéphane Grolleau (IMN) for his expert tutoring on the use of the granulometry device. We also thank AREVA NP for the supply of graphite samples.

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