



Optimization of Brazilian TNT industry wastewater treatment using combined zero-valent iron and fenton processes

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ABSTRACT

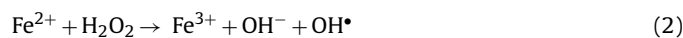
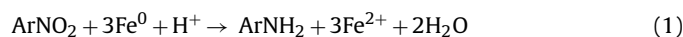
This work explores the optimization of combined zero-valent iron and fenton processes for the treatment of TNT industry wastewater, a residue with recognized polluting potential due to its high concentration of 2,4,6-trinitrotoluene and extremely acidic pH due of the nature of the product purification process. The results of the optimization study indicate that the most efficient condition for reducing the concentration of TNT also generates sufficient amounts of iron(II) for the subsequent oxidative treatment through the Fenton reaction. In general, it was observed that the treatment was highly efficient in terms of meeting the main associated environmental parameters, since it reduced acute toxicity, removed 100% of TNT, 100% of the organic nitrogen and 95.4% of the COD.

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1. Introduction

With a global production estimated at 108 tons/year, nitroaromatic compounds are used intensively in several different industrial segments, including for production of inks, plastics, pharmaceutical and veterinarian products, dyes, polyurethane foams, herbicides, insecticides and explosives [1]. These compounds are generally recalcitrant to biological treatment and constitute a source of pollution due to both their toxic and their mutagenic effects on humans, fish, algae and microorganisms [2–5]. The main source of nitrocompound contamination is associated with industrial processes, storage operations and use in military installations [1,2]. The discharge of residues generated during explosive manufacturing and processing as well as the associated level of contamination varies widely, depending on the intensity of the manufacturing operations and the effectiveness of the technologies used to treat the residues [6]. Within this context, conventional biological wastewater treatment processes (e.g., activated sludge) are not effective in treating the residues because the electron-withdrawing nitro constituents in these explosives inhibit the electrophilic attack through enzymes [7]. Chemical oxidation methods (e.g., advanced oxidation processes) are also not considered effective because the nitrofunctional groups inhibit oxidation [8]. Currently, one of the more commonly used methods is incineration. Although efficient, its applicability is questioned due to the emission of gaseous pollutants [7]. Recent

studies have shown that TNT could be biologically transformed into triaminotoluene (TAT) through intermediates (e.g., aminonitrotoluenes and hydroxyaminotoluenes) using pure and mixed cultures under anaerobic conditions [9,10]. In these studies, it was found that TAT was unstable and could be transformed into phenolic products, depending on the pH. These compounds were further degraded abiotically into formaldehyde, methanol, nitrous oxide and water [11]. Additionally, some researchers have considered that reductive processes mediated by iron wool can facilitate the conventional treatments of nitroaromatic compounds due to their transformation into composites of a larger biodegradability [12–15].



This work presents the study and optimization of combined zero-valent iron (iron wool) phenolic products and Fenton processes for the treatment of TNT industry wastewater, which is a residue called yellow water with recognized polluting potential due to its high 2,4,6-trinitrotoluene concentration and extremely acidic pH resulting from the nature of its manufacturing process. The central idea of this work was to use the physical–chemical characteristics of the effluent to enhance the treatment efficiency. In other words, in addition to promoting a reduction of the 2,4,6-trinitrotoluene in chemical species with an increased susceptibility to oxidative degradation as aminoaromatic compounds, the acid leaching process promoted by the effluent can also generate sufficient amounts of iron(II) in an acid solution, thereby satisfying the necessary conditions for complement-

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ing this treatment through the Fenton reaction (Eqs. (1) and (2)).

2. Material and methods

2.1. Chemicals and supplies

All chemicals were of analytical grade or higher and were purchased from Merck or Sigma reagent. The samples of wastewater were collected at IMBEL, Belics Materials Industry, located in São Paulo State, Brazil. The wastewater originating from preliminarily washings involved in the TNT purification process. This effluent is also called yellow water and has a pH 1.0, COD of 638 mg L^{-1} and 156 mg L^{-1} of 2,4,6-trinitrotoluene [2].

2.2. Iron wool

For characterization effects, the X-ray fluorescence of the iron wool was analyzed. It was verified that it is composed primarily of iron ($98.53 \pm 0.05\%$), presenting, however, other components in smaller proportions, such as carbon ($0.1 \pm 0.05\%$), Mn ($0.8 \pm 0.05\%$), S ($0.13 \pm 0.05\%$), Ca ($0.12 \pm 0.05\%$), Cr ($0.11 \pm 0.05\%$) and Cu ($0.04 \pm 0.05\%$). For the treatment studies, the iron wool was acquired in normal local sales outlets and used without any prior treatment or purification.

2.3. Analytical control

The following parameters were used to determine the pollution potential of the effluent and ensure analytic control of the system.

2.3.1. Liquid chromatography analysis

TNT decay was followed by reversed phase liquid chromatography. The HPLC consisted of a LC Shimadzu pump 10AT equipped with a UV detector selected at $\lambda = 254 \text{ nm}$ and fitted with a LiChrosphere RP-18 column $250 \text{ mm} \times 4.6 \text{ mm}$ i.d., $5 \mu\text{m}$ particle size (Merck). The system was operated in isocratic mode (methanol/water; 60/40, v/v) at a flow rate of 1 mL min^{-1} . The retention time of the TNT under these conditions was 9.4 min ($\pm 0.5 \text{ min}$).

2.3.2. Chemical oxygen demand (COD)

A sample was refluxed in a strongly acid solution with a known excess of $\text{K}_2\text{Cr}_2\text{O}_7$. The consumed oxygen was measured against the standard at 600 nm with a spectrophotometer [16].

2.3.3. Total phenol

The total phenol was measured following the standard procedures described by APHA—American Public Health Association [16]. A total of $250 \mu\text{L}$ of a carbonate–tartarate solution (12 g L^{-1}) and $25 \mu\text{L}$ of Folin–Ciocalteus were added separately to $1000 \mu\text{L}$ of effluent. The total phenol was quantified by spectrometry (700 nm) using an analytical curve.

2.3.4. Organic nitrogen

The study used the Kjeldahl method (micro-Kjeldahl) for determining the organic nitrogen present in the effluent yellow water. This method involves calculating the nitrogen content in the sample through the intent sulfuric acid digestion and posterior distillation of the ammonia, which is fixed in an acid solution and titulated [16].

2.3.5. Iron(II) determination

This procedure primarily involved the reduction of the iron with hydroquinone and the sequential reaction with o-fenantroline, forming a complex color, which was measured

using a Hitachi U-2000 spectrophotometer in the 510 nm region ($\epsilon = 1.2 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) [16].

2.4. Treatment conditions

The treatability experiments with yellow water effluent were conducted in an orbital table with 500 mL Erlenmeyer bottles with agitation of 100 rpm and temperature control at 20°C . Each Erlenmeyer bottle was filled with 250 mL of effluent with a different pH (1.6, 3.0, 5.0, 7.0 and 8.3), amounts of metallic iron (0, 0.2, 0.6, 1.0 and 1.3 g) and reaction times (0, 6, 15, 24 and 30 min) according to the experimental design described in Section 2.5. Due to the fact that the effluent is made of course acid, $\text{NaOH } 6 \text{ mol L}^{-1}$ was used to adjust the pH. After this treatment, the TNT and Fe(II) concentration results were analyzed to determine the efficiency and calculate the Fenton treatment planning. The Fenton treatment was completed using residual Fe(II) with the addition of the hydrogen peroxide ($30\% \text{ H}_2\text{O}_2$ solution and $\text{Fe}^{2+} : \text{H}_2\text{O}_2$ ratio of 1:5) on the reaction half with constant agitation for 30 min in darkness. After the treatability assays, the pH sample was corrected to 7.0 ± 0.05 for characterization analyses.

2.5. Optimization of yellow water treatment

The experiments were arranged according to an experimental design using response surface methodology (RSM) to reveal the effect of pH, retention time, concentration of metallic iron and the interaction between these factors on the selected reply (TNT concentration reduction). For each factor, the researchers selected high and low set points coded into $+1.682$, $+1$, 0 , -1 and -1.682 , respectively. A quadratic model was used to adjust the studied experimental results, considering only the variables that presented a significant effect. The statistical analysis was performed using *STATGRAPHICS Plus* statistical software—Version 4.1.

3. Results and discussion

The study of the yellow water effluent treatment process was conducted in two stages. Initially, its treatment with iron wool was optimized to establish the conditions for achieving the largest reduction in the TNT concentration. It was observed that this process is related to the pH of the effluent. Because the pH is significantly acidic, it also favored the leaching of the iron wool, which supplied sufficient amounts of iron(II) in solution for a later oxidative treatment through the fenton reaction.

Aiming to establish the best treatment conditions for the nitroaromatic compound degradation, the researchers employed 16 different treatments (Table 1), in which the evaluated response was the reduced concentration or conversion of TNT (%), which was analyzed by HPLC.

The evaluation statistics associated with the effect of pH, the retention time, the concentration of the iron wool, as well as how the interaction between such factors affected the selected reply was analyzed with the aid of the program *Statgraphics Plus/Windows 4.1*. Fig. 1 (Pareto chart) shows each of the estimated effects and interactions in decreasing order of importance, where the vertical line defines 95% of the reliable interval ($p = 0.05$).

This test showed that, for the conversion of 2,4,6-trinitrotoluene, all the variables [A], [B] and [C] and the quadratic effect $[B]^2$ had significant effect. The quadratic effect of interaction [AB], [AC] and [BC] and $[A]^2$ and $[C]^2$ effect were not significant. According to Bell et al. [15], the reduction of TNT is dependent on H^+ , which justifies the negative effect of the [A] variable. On the other hand, the effect of the reaction time [B] and iron wool [C] had a positive influence on the TNT conversion. Using the significant effects, it was possible to adjust a quadratic model to explain the TNT conversion, as shown

Table 1
Matrix of the factorial planning and responses obtained in the studies of the yellow water effluent treatment with the wool metallic iron.

| Experiment | pH | RT (min) | wmi (g) | Responses | |
|------------|-----|----------|---------|--------------------|------------------------------|
| | | | | TNT conversion (%) | Fe(II) (mg L ⁻¹) |
| 1 | 5.0 | 15.0 | 0.6 | 63.0 | 63.0 ± 2 |
| 2 | 3.0 | 24.0 | 0.2 | 61.0 | 54.0 ± 2 |
| 3 | 7.0 | 24.0 | 0.2 | 21.0 | 34.0 ± 2 |
| 4 | 5.0 | 15.0 | 1.3 | 31.1 | 66.0 ± 2 |
| 5 | 3.0 | 6.0 | 0.2 | 42.7 | 59.0 ± 2 |
| 6 | 5.0 | 15.0 | 0.0 | 0.0 | 0.00 |
| 7 | 5.0 | 30.0 | 0.6 | 69.6 | 65.0 ± 2 |
| 8 | 3.0 | 6.0 | 1.0 | 47.3 | 69.0 ± 2 |
| 9 | 3.0 | 24.0 | 1.0 | 89.0 | 102.0 ± 2 |
| 10 | 7.0 | 6.0 | 0.2 | 12.0 | 24.0 ± 2 |
| 11 | 7.0 | 24.0 | 1.0 | 42.0 | 29.0 ± 2 |
| 12 | 8.3 | 15.0 | 0.6 | 79.0 | 31.0 ± 2 |
| 13 | 5.0 | 0.0 | 0.6 | 0.0 | 0.00 |
| 14 | 8.3 | 15.0 | 0.6 | 59.0 | 23.0 ± 2 |
| 15 | 7.0 | 6.0 | 1.0 | 20.0 | 29.0 ± 2 |
| 16 | 5.0 | 15.0 | 0.6 | 62.0 | 33.0 ± 2 |

Legend—RT: reaction time, wmi: wool metallic iron.

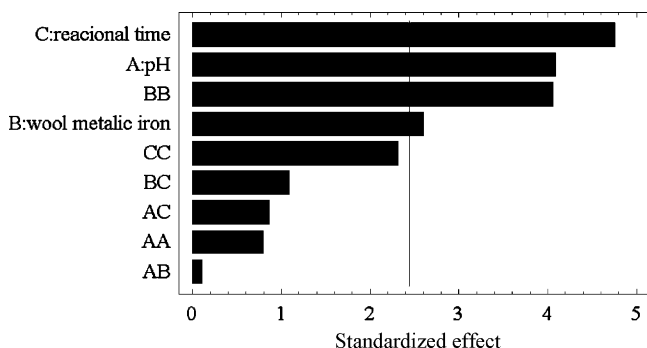


Fig. 1. Pareto chart for standardized effects. Estimated effects for pH, reaction time and iron wool. The vertical line defines 95% of the reliable interval ($p=0.05$).

in Eq. (3).

$$\% \text{ [TNT] reduction} = 10.493 - 10.937 \times (\text{pH}) + 123.087 \times (\text{iw}) + 5.267 \times (\text{rt}) + 0.775 \times (\text{pH})^2 - 98.665 \times (\text{iw})^2 \quad (3)$$

where pH = effluent pH; rt = reaction time (min); iw = iron wool (g).

In this way, the model was adjusted considering the variable presenting a significant effect. In this case, an ANOVA table was constructed for the adopted model, which was used to statistically analyze the results (Table 2).

The ANOVA table partitions the variability in TNT conversion into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square

Table 2
Analysis of variance for TNT conversion.

| Variance source | Sum of squares | Df | Mean square | F-ratio | p-value |
|-----------------------|----------------|----|-------------|---------|---------|
| A: pH | 2336.61 | 1 | 2336.61 | 16.73 | 0.0064* |
| B: wool metallic iron | 948.61 | 1 | 948.61 | 6.79 | 0.0403* |
| C: reaction time | 3166.97 | 1 | 3166.97 | 22.68 | 0.0031* |
| AA | 89.15 | 1 | 89.15 | 0.64 | 0.4548 |
| AB | 1.62 | 1 | 1.62 | 0.01 | 0.9177 |
| AC | 105.12 | 1 | 105.12 | 0.75 | 0.4190 |
| BB | 2308.72 | 1 | 2308.72 | 16.53 | 0.0066 |
| BC | 165.62 | 1 | 165.62 | 1.19 | 0.3180 |
| CC | 747.14 | 1 | 747.14 | 5.35 | 0.0600 |
| Total error | 837.96 | 6 | 139.66 | | |
| Total (corr.) | 11,277.9 | 15 | | | |

* Significantly at the 95.0% confidence level.

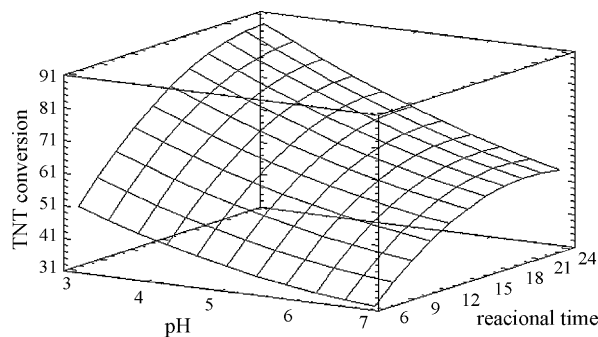


Fig. 2. Response surface and level curve described for Eq. (3) relating the effects of pH and reaction time during the conversion of TNT into effluent.

against an estimate of the experimental error. In this case, four effects have p -values of less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level. The R^2 statistic indicates that the model as fitted explains 92.57% of the variability in TNT conversion. The adjusted R^2 statistic, which is more suitable for comparing models with different numbers of independent variables, is 81.42%. The standard error of the estimate shows the standard deviation of the residuals to be 11.82. The mean absolute error (MAE) of 5.58 is the average value of the residuals. The Durbin–Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in the data. Since the DW value is greater than 1.4, there is probably not any serious autocorrelation in the residuals.

The model was considered satisfactory by all means, presenting high values of adjustment regression to a 95% confidence level, suggesting that Eq. (3) was adjusted to describe the TNT conversions [17].

Response surfaces were constructed to show the estimate for TNT conversion into effluent in function of the significant variables. In the response surface of Fig. 2, which relates the conversion (or concentration reduction) of TNT into effluent to the reaction time (or retention time) and pH, the iron wool variable was fixed at level zero.

We can observe that the increased reaction time and reduced pH favored the TNT conversion. However, for shorter times (less than 6 min), as well as for longer times (above 21 min), the low pH proved to be more efficient than the pH that increased during TNT conversion, characterizing the representative area of improved efficiency shown in Fig. 2. Within this context, the conditions of improved efficiency (89% of the conversion) can be represented by pH 3, and multiplied by 24 min.

The response surface of Fig. 3 relates how pH and iron wool mass affect the reduction of the TNT concentration. The reaction time was

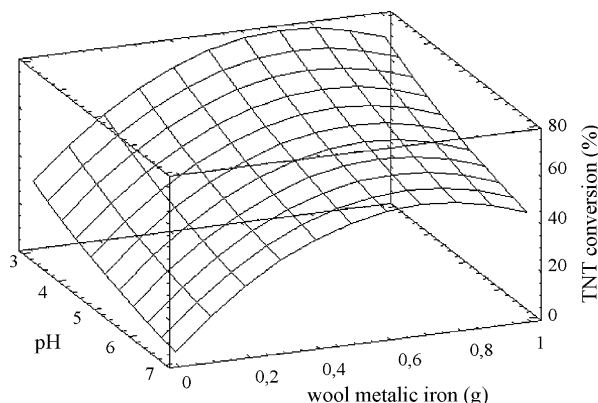


Fig. 3. Response surface and level curve described for Eq. (3) relating the effects of iron wool mass and pH during the conversion of TNT into effluent.

Table 3
Results for the treatability study for TNT wastewater.

| | pH | COD (mg L ⁻¹) | Organic nitrogen (mg L ⁻¹) | Total phenol (mg L ⁻¹) | TNT (mg L ⁻¹) |
|-------------|------------|---------------------------|--|------------------------------------|---------------------------|
| Untreated | 3.0 ± 0.03 | 638 ± 12 | 729 ± 60 | 0.048 | 156 ± 1 |
| Post-wmi | 3.2 ± 0.05 | 619 ± 15 | 697 ± 60 | 0.045 | n.d |
| Post-fenton | 7.0 ± 0.03 | 29 ± 12 | n.a | 0.059 | n.a |

n.d.: non-detected, n.a.: non analyzed, post-wmi: after wool metallic iron treatment, post-fenton: after fenton treatment.

fixed at level zero. We can observe that the increased effluent pH has a negative influence when it comes to converting TNT into any iron wool mass, and positive for low pH (pH lathe band of three) characterizing, under these conditions, a maximum efficiency of approximately 0.8–1 g iron wool.

The point that produced the most efficient TNT conversion (80%) was at pH 3 and with an iron wool mass of approximately 0.8 g/250 mL or 3.2 g L⁻¹. This can be better observed through the level curve of the surface (Fig. 3). The response surface of Fig. 4 relates the effect of the reaction time and the iron wool with the reduced TNT concentration, with the pH variable fixed at level zero.

We can clearly observe that the increased time (above 24 min) together with the increased masses (approximately 0.6–1.0 g) correspond to relatively more favorable conditions. Within this context, the point that obtained the greatest TNT conversion (66%) used the mass of 0.8 g/250 mL. This behavior can be better observed through the level curve of the surface (Fig. 4).

A statistical study of the surfaces of answers determined within the studied levels was used to determine the treatment conditions that provide the greater conversion of TNT into effluent. In a generalized manner, it was possible to conclude that the conditions that contributed most to the effective primary treatment of the effluent were those that used pH acid (1 and 3), an iron wool mass between 0.6 and 1 g/250 mL with reaction times of more than 25 min. Experiment 9 of the matrix in experimental design (Table 1) also illustrates this condition in a more efficient fashion. Within this context, treatment under these conditions was repeated for generally larger amounts of effluent for the second stage of the research. It is important to point out that in the effluent treatment, the average concentration of joined iron (Fe²⁺) was 100 mg L⁻¹.

3.1. Preliminary assay of Fenton treatment for the yellow water effluent

For the Fenton treatment, the researchers used the Fe²⁺:H₂O₂ ratio of 1:5 or 100 mg L⁻¹ of iron and 500 mg L⁻¹ of H₂O₂. According to OH et al. [18], this ratio represents an excellent condition for the degradation of TNT solutions and other nitroaromatic compounds. Within the experimental context, a treatment for 120 min in Erlenmeyer under 100 rpm agitation was used. The relative results for this treatment are shown in Table 3.

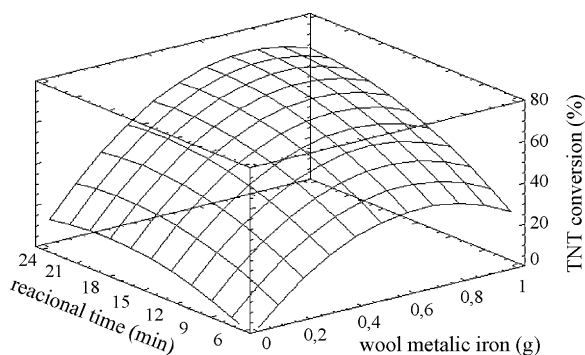


Fig. 4. Response surface and level curve described for Eq. (3) relating the effects of iron wool mass and reaction time during the conversion of TNT into effluent.

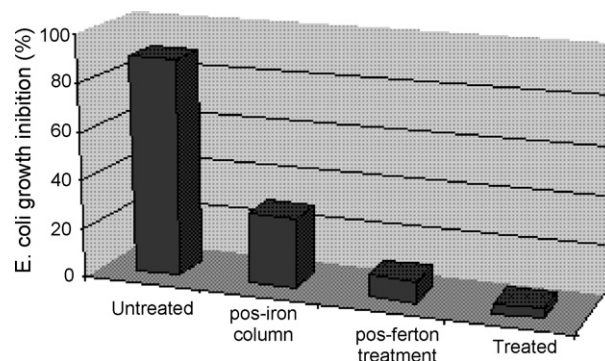


Fig. 5. Inhibition of *E. coli* growth in the presence of treated and untreated effluents.

In general terms, it was observed that although the iron wool treatment reduced all the TNT concentrations, it does not have any other significant effect on the effluent. However, when combined with the fenton treatment, it promoted extensive changes in several parameters of the effluent, removing 100% of the TNT, 100% of the organic nitrogen and 95.4% of the COD (Table 3). The total phenol practically does not change after treatment with iron wool, but increases 23% after the fenton treatment. This behavior can be explained by the addition of the radicalar mechanism, typical of advanced oxidative processes. Furthermore, it is important to point out that treatment attempts for this effluent using fenton or photo-fenton processes under the adopted conditions (Fe²⁺ relation:H₂O₂ of 1:5 or 100 mg L⁻¹ and 500 mg L⁻¹ of H₂O₂) did not significantly remove TNT, total nitrogen or COD, strengthening the hypothesis that treatment with the iron wool forms chemical species with increased biodegradability, which are more easily degraded by the fenton process. Fig. 5 shows that all the stages of the treatment reduced the acute toxicity of the effluent.

Comparatively, the treatment with iron wool generated the largest reduction (approximately 40%), which can be associated with the complete conversion of the 2,4,6-trinitrotoluene into relatively less toxic chemical species. The reduction promoted by the fenton treatment was smaller, although in terms of neutralization, the acute toxicity of the effluent was already approximately 5%, which compared with other effluents, is relatively low. For example, using this exact bioindicator, Souza et al. [19] observed an inhibition of 1.59% in a treated pulp effluent produced by the nitrocellulose industry.

4. Conclusion

The optimization of the treatment using the iron wool and fenton process has proven to have the conditions to fully convert TNT into effluent. Moreover, this experimental condition generated sufficient concentrations of residual iron for the fenton reaction, reducing the acute toxicity, removing 100% of TNT, 87.5% of the total phenols, 100% of the total nitrogen and 95.4% of the COD. The main advantage of the treatment seems to be associated with the primary conversion of the 2,4,6-trinitrotoluene in chemical species with a greater susceptibility to oxidative degradation, consecutively promoted for the Fenton reaction, that, in spite of not promoting

the total TNT mineralization, significantly reduces toxicity. We conclude that this process can be considered highly promising for the treatment of effluents from the TNT production industry, with sufficient quality for release into the receiving body without causing damage to the same. After complementary studies, the final product could be used as industrial reuse water for the explosive industry itself.

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