

# Wet peroxide oxidation and catalytic wet oxidation of stripped sour water produced during oil shale refining

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## Abstract

Catalytic wet oxidation (CWO) and wet peroxide oxidation (WPO) of stripped sour water (SSW) from an oil shale refinery was investigated. Greater than 70% total organic carbon (TOC) removal from SSW was achieved using  $\text{Cu}(\text{NO}_3)_2$  catalysed WO under the following conditions using a glass lined reaction vessel: 200 °C,  $p\text{O}_2 = 0.5$  MPa, 3 h,  $[\text{Cu}(\text{NO}_3)_2] = 67$  mmol/L. Significant TOC removal (~31%) also occurred in the system without added oxygen. It is proposed that this is predominantly due to copper catalysed oxidative decarboxylation of organics in SSW based on observed changes in copper oxidation state. Greater than 80% TOC removal was achieved using WPO under the following conditions: 150 °C,  $t = 1.5$  h,  $[\text{H}_2\text{O}_2] = 64$  g/L. Significantly more TOC could be removed from SSW by adding  $\text{H}_2\text{O}_2$  in small doses as opposed to adding the same total amount in one single dose. It was concluded that WPO was a far more effective process for removing odorous compounds from SSW. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Catalytic wet oxidation; Oil shale; Stripped sour water; Wet peroxide oxidation

## 1. Introduction

The management of aqueous, organics-laden waste streams is an issue confronting many chemical, food, pharmaceutical and refining industries today [1–4]. The refinement of oil shale is a multi-billion dollar world-wide industry that faces such a problem. Although this is a multi-billion dollar industry, its sustainability depends greatly on the environmental impacts of the refining process. The oil shale refining process that was used in Gladstone, Australia, which utilised Alberta-Taciuk Processor (ATP) technology produced an aqueous wastewater (retort water) at the rate of approximately 20 m<sup>3</sup>/kTonne of product/hour that contained a high concentration of phenols, pyrroles, organic acids and a host of other organics that are ill-defined. This wastewater is steam stripped to remove ammonia and hydrogen sulphide after which the water is known as Stripped Sour Water (SSW). The SSW produced at Gladstone

has a total organic carbon (TOC) loading of ~9 g/L and a chemical oxygen demand (COD) of 18 g/L and requires treatment prior to discharge. Very little research has been conducted on the removal of organics from wastewaters produced during oil shale refining however due to increasing environmental awareness and increased interest in alternative fuel sources, methods for treating these waters are becoming important.

Of the various processes that can be used to remove organics from wastewaters, processes that do not produce any waste products are receiving increased interest as many industries are trying to reduce the amount of waste generated. Two wastewater treatment processes that can produce minimal waste when 100% organics oxidation is achieved and the catalyst and/or oxidant used are efficiently removed from the treated process stream are catalytic wet oxidation (CWO) and wet peroxide oxidation (WPO). The CWO process removes organics by completely oxidising them to carbon dioxide and water, in the liquid phase, using oxygen or air in the presence of a catalyst, while the WPO process involves complete oxidation of organics in the liquid phase using hydrogen peroxide. A significant amount of research has been conducted on CWO and the development of catalysts for use in CWO over the last three decades [4,5]. A number of these studies have focussed on the CWO of acetic acid [6–8]

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and phenol [9–11], while a number of studies have also been conducted using actual industrial streams such as Bayer liquor [12,13], distillery wastewater [14,15] and dyeing and printing wastewater [16]. WPO has also been studied by a number of researchers [17–20].

The main aim of this study was to investigate the removal of organics from SSW using the two aforementioned processes, CWO and WPO. Based on our previous studies on CWO of SSW which showed that  $\text{Cu}(\text{NO}_3)_2$  was a far superior catalyst than nitrate salts of other transition metals (Fe, Co, Mn, Ni) [21]  $\text{Cu}(\text{NO}_3)_2$  catalysed WO of SSW was investigated in detail to gain a better understanding of the mechanism of  $\text{Cu}(\text{NO}_3)_2$  catalysed WO of stripped sour water, and to determine the optimum reaction conditions for this catalyst. The reaction conditions used in this study (oxygen partial pressure, temperature, pH and stirrer speed used are optimal values determined from previous studies [21]). With the stirrer speed and oxygen partial pressure used the rate determining step in CWO of SSW is the chemical reaction between the organic compounds present and the catalyst/oxygen.

Development of an environmentally friendly process for treating SSW would lead to a significant reduction in the environmental impacts of the oil shale refining process.

## 2. Materials and methods

### 2.1. CWO experiments

CWO experiments were carried out in a continuously stirred, 1.2 L, stainless steel 316 autoclave (Parr Autoclave, Moline IL, USA), which had fittings to enable gas addition to the liquid phase and liquid sampling. In the standard reaction, a specific amount of required catalyst ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (99.5%, BDH Chemicals) or  $\text{CuO}$  (99+%, Merck) was dissolved in 0.6 L of SSW, which was provided by Southern Pacific Petroleum. After acidification with 36% HCl (Ajax Finechem) to pH 3 the solution was placed in the reactor vessel together with a pre-determined amount of free-radical inhibitor (t-butanol (99.9% Ajax Chemicals) or promoter (hydroquinone (>99% BDH Chemicals)) where necessary. The vessel was sealed and the headspace area was evacuated to approximately 14 kPa. The vessel and its contents were then heated to 200 °C with the stirrer set at 800 rpm. Once the target temperature was reached, oxygen was introduced and maintained at a constant partial pressure of 0.5 MPa ( $P_{\text{O}_2}$ ) for the duration of the test.

### 2.2. WPO experiments

WPO experiments were carried out in the same reactor as described above using the same volume of SSW. The required quantity of  $\text{H}_2\text{O}_2$  (30% w/v, AnalaR, Merck Pty Ltd) was then delivered into the vessel using a Lab Alliance Series II high-pressure HPLC pump. The stoichiometric amount of  $\text{H}_2\text{O}_2$  required was calculated based on the following rudimentary equation,  $\text{C} + 2\text{H}_2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ , where all TOC present in SSW was assumed to be present as C. Samples were withdrawn at pre-determined time periods.

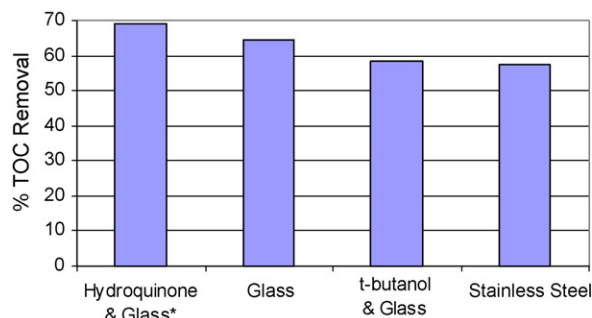


Fig. 1. Effect of hydroquinone, t-butanol and reaction vessel surface on CWO of SSW. Conditions:  $T=200\text{ }^\circ\text{C}$ ,  $t=3\text{ h}$ ,  $p_{\text{O}_2}=0.5\text{ MPa}$ ,  $\text{pH}_i=3$ ,  $\text{Cu}(\text{NO}_3)_2=33.33\text{ mmol/L}$ . \*Glass insert was placed inside SS autoclave reaction vessel.

### 2.3. Analytical

TOC was analysed using an O.I Analytical Model 1010 Total carbon analyser. pH measurements were taken using a Metrohm 620 pH meter.

## 3. Results and discussion

### 3.1. Catalytic wet oxidation of SSW

#### 3.1.1. Effect of promoter, inhibitor and reaction vessel surface material

The effect of a promoter (hydroquinone), inhibitor (t-butanol) and the reaction vessel surface material on  $\text{Cu}(\text{NO}_3)_2$  catalysed WO of SSW was investigated to gain information on the reaction mechanism and to investigate the optimum reaction conditions. The results of these tests are presented in Fig. 1. The slight improvement in TOC removal using a glass vessel (compared to stainless steel) and slight decrease in TOC removal that occurred when an inhibitor was added to the system indicates that free radical reactions are involved in  $\text{Cu}(\text{NO}_3)_2$  catalysed WO of the SSW. The effect of the inhibitor and promoter was quite low indicating that oxidation via free radicals is a minor mechanism for this system or the promoter and inhibitor were not highly suitable compounds for this system. Based on the improved TOC removal obtained using the glass vessel this method was selected for future tests.

#### 3.1.2. $\text{Cu}(\text{NO}_3)_2$ catalysed oxidation of SSW in absence of oxygen

Close examination of data from  $\text{Cu}(\text{NO}_3)_2$  loading tests conducted previously [21] showed that significant TOC removal from SSW occurred during the heat-up period despite the lack of oxygen (Fig. 2). Hence it was decided to investigate this more closely to determine the maximum amount of TOC that could be removed from SSW using only  $\text{Cu}(\text{NO}_3)_2$  and heat, and also to investigate the mechanism of this removal. The maximum amount of TOC that could be removed was approximately 31% in approximately 1 hour in the presence of  $\text{Cu}(\text{NO}_3)_2$  as opposed to approximately 10% without added  $\text{Cu}(\text{NO}_3)_2$  (Fig. 3). Hence approximately 21% of the TOC in SSW was able to be removed due to the presence of  $\text{Cu}(\text{NO}_3)_2$ , indicating that copper and/or

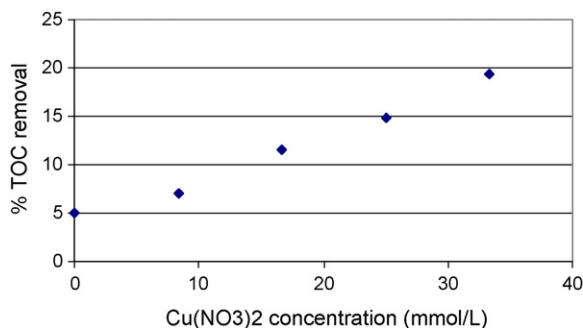


Fig. 2. Effect of increasing  $\text{Cu}(\text{NO}_3)_2$  loading on TOC removal in the absence of oxygen. Conditions: final  $T=200^\circ\text{C}$ ,  $t\sim 30$  min,  $p\text{O}_2=0.5$  MPa,  $\text{pH}_i=3$ .

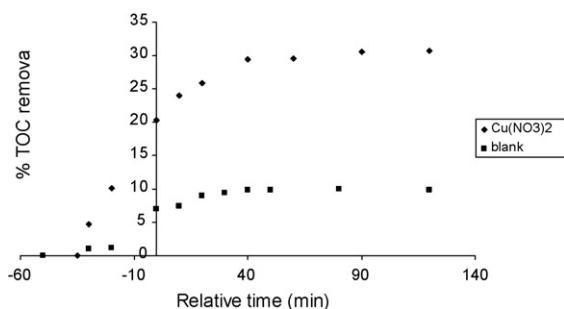


Fig. 3. TOC removal with and without  $\text{Cu}(\text{NO}_3)_2$  with no added oxygen. Conditions:  $T=200^\circ\text{C}$ ,  $\text{pH}_i=3$ ,  $\text{Cu}(\text{NO}_3)_2=41.7$  mmol/L.  $P_{T\geq 0}=1.6$  MPa.

nitrate are capable of direct oxidation of a significant amount of the TOC in SSW. Imamura and co-workers [22] have previously reported that  $\text{Cu}(\text{NO}_3)_2$  can oxidise acetic acid in the absence of oxygen, and that the extent of oxidation increases with increasing  $\text{Cu}(\text{NO}_3)_2$  concentration. Imamura and co-workers [22] attributed the oxidation of acetic acid to oxidation by nitrate ion. The mechanism proposed by Imamura and co-workers [22] was thought to play a significant role in the SSW/ $\text{Cu}(\text{NO}_3)_2$  system however based on visual observations of the colour of SSW (Fig. 4) before treatment (brown), immediately after treatment (yellow) and approximately 1 hour after treatment when left in air (green) which supported a change in copper oxidation state from 2+ to 1+ during the reaction, and back to 2+ when the solution was exposed to air it was clear that copper also played a role in this system (Imamura and co-workers [22] did



Fig. 4. SSW colour during test conducted with  $\text{Cu}(\text{NO}_3)_2$  in absence of oxygen. (samples left to right: (1) SSW at beginning of test, (2) SSW immediately after completion of test, (3) SSW after exposure to air for  $\sim 1$  h).

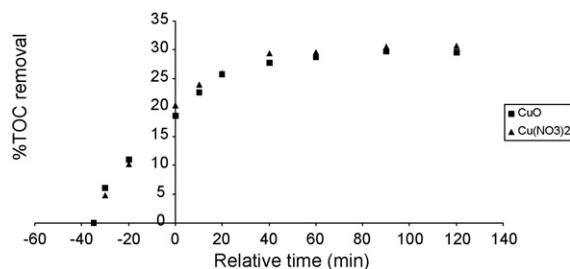


Fig. 5. TOC removal with  $\text{Cu}(\text{NO}_3)_2$  and  $\text{CuO}$  catalysts with no added oxygen. Conditions:  $T=200^\circ\text{C}$ ,  $\text{pH}_i=3$ ,  $\text{Cu}=41.7$  mmol/L.  $P_{T\geq 0}=1.6$  MPa.

not report any change in copper oxidation state in their study). To investigate the contribution of the nitrate ion (and copper) to the high TOC removal that was achieved using  $\text{Cu}(\text{NO}_3)_2$  a test was conducted using  $\text{CuO}$ . The results of the test using  $\text{CuO}$  are presented in Fig. 5. It can be seen that very similar TOC removal was achieved in the absence of oxygen using both the  $\text{Cu}(\text{NO}_3)_2$  and  $\text{CuO}$  catalysts, while similar colour changes were also observed to take place for both systems (colour changes were also confirmed by UV-Vis analysis of solutions). These results support that nitrate ion had no significant role in the removal of TOC from SSW in the  $\text{Cu}(\text{NO}_3)_2$  system, at least in the absence of  $\text{O}_2$ . A possible mechanism that would account for the significant TOC losses that occurred due to direct oxidation of SSW organics by  $\text{Cu}(\text{NO}_3)_2$  and  $\text{CuO}$  in the absence of oxygen is copper catalysed decarboxylation. Copper is a well known catalyst for decarboxylation reactions of compounds such as keto acids and aliphatic carboxylic acids [23,24]. To the best of our knowledge this mechanism has not previously been proposed to occur during CWO of wastewaters using homogenous copper salts. This is surprising considering the number of studies that have been conducted using copper salts as WO catalysts [22,25–30]. Another mechanism which may have also contributed to TOC removal is precipitation of copper-organic complexes. However based on the significant copper oxidation state changes observed it most likely that copper catalysed decarboxylation is the predominant mechanism.

The high extent of TOC removal in the system without oxygen supports the results discussed in Section 3.1.1 where a promoter and inhibitor did not have a large effect on TOC removal from

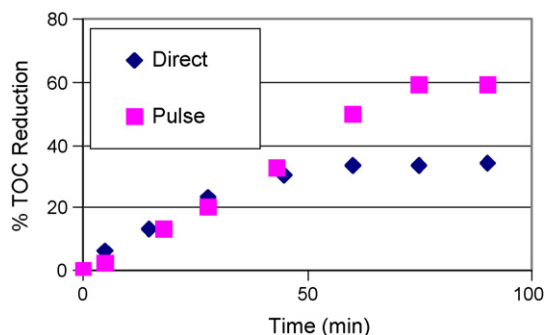


Fig. 6. Effect of single versus multiple additions of  $\text{H}_2\text{O}_2$ . Conditions: 1.5 h, 125 °C,  $\text{pH}_i$  3.5, total  $\text{H}_2\text{O}_2$  added = 51 g/L (6 equal additions at 0,7,12, 20, 30 and 45 min for pulse test).

SSW in the oxygenated system. This is due to a significant amount of the TOC removal in the oxygenated system also most likely occurred via copper catalysed decarboxylation and hence free radical based reactions accounted for a significantly lower proportion of the total TOC removal observed.

### 3.2. Wet peroxide oxidation of SSW

#### 3.2.1. Effect of $\text{H}_2\text{O}_2$ delivery – single addition versus multiple additions

The method of addition of  $\text{H}_2\text{O}_2$  to SSW was investigated. The two different methods used were a single addition method and a multiple addition method (same total amount of  $\text{H}_2\text{O}_2$  added). The results of these tests are presented in Fig. 6. The addition of the same total amount of  $\text{H}_2\text{O}_2$  using a number of small doses as opposed to using one single dose was clearly a more effective method for removing TOC from SSW with approximately 23% more TOC removal being achieved using the multiple addition method. The higher TOC removal achieved using multiple small doses is most likely due to a higher portion of  $\text{H}_2\text{O}_2$  degrading into non-oxidising species in the test using a single large dose and hence being “wasted”.

#### 3.2.2. Effect of temperature

The effect of temperature on TOC removal using WPO is presented in Fig. 7. TOC removal increased with increasing temperature from 100 to 150 °C, while a further increase in temperature from 150 to 175 °C however led to a decrease in TOC removal. The effect of temperature on TOC removal indicates there is a delicate balance between:

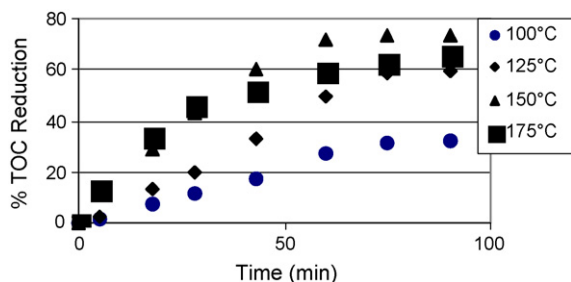


Fig. 7. Effect of temperature on WPO of SSW. Conditions:  $\text{pH}_i$  3.5, total  $\text{H}_2\text{O}_2$  added = 51 g/L (6 equal additions at 0,7,12, 20, 30 and 45 min).

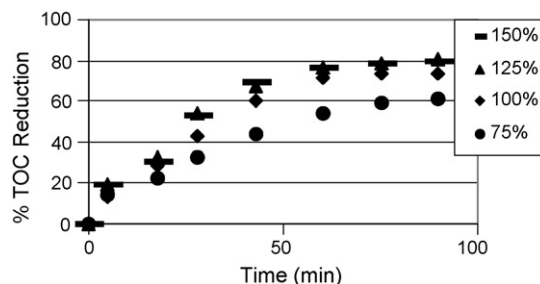


Fig. 8. Effect of  $\text{H}_2\text{O}_2$  dose (% of approximate stoichiometric quantity required – see legend) on TOC removal. Conditions:  $T = 150$  °C,  $\text{pH}_i$  3.5,  $\text{H}_2\text{O}_2$  dose points at 0,7,12, 20, 30 and 45 min.

- The activation energy required for reaction between the organics in SSW and the oxidising species produced from  $\text{H}_2\text{O}_2$  (predominantly hydroxyl radicals)
- The energy required to convert  $\text{H}_2\text{O}_2$  into oxidising species, and the rate at which they are produced
- The rate of reaction between the oxidising species produced from  $\text{H}_2\text{O}_2$  and organics in SSW

Hence at 150 °C the combined aforementioned energies / rates lead to optimum TOC removal. The assertion in point one given above that the mechanism of WPO of SSW occurs predominantly via hydroxyl radicals is supported by tests conducted using only oxygen as an oxidant under the following reaction conditions,  $\text{PO}_2 = 500$  kPa,  $t = 180$  min,  $\text{pH}_i = 3$  where TOC removal was 9% and 14% using temperatures of 150 °C and 175 °C respectively [31]. Based on the aforementioned data oxidation due to  $\text{O}_2$  produced from  $\text{H}_2\text{O}_2$  degradation in the WPO systems studied could not have been predominantly responsible for the levels of TOC removal observed.

#### 3.2.3. Effect of dosage

The effect of  $\text{H}_2\text{O}_2$  dose on WPO of SSW is presented in Fig. 8. TOC removal increased with increasing dosage up to 125% of the approximated stoichiometric amount of  $\text{H}_2\text{O}_2$  required, where approximately 80% of TOC was removed. A further increase in dosage to 150% did not lead to any further increase in TOC removal.

#### 3.2.4. Colour

A significant change in SSW colour, from orange to dark brown, occurred within the first five minutes of all WPO tests conducted at temperatures above 100 °C. The colour changes that occurred during the WPO test at 150 °C are shown in Fig. 9. The change in colour that occurred in the first five minutes was most likely due to the formation of compounds such as o-benzoquinone, p-benzoquinone and coloured condensation products from the oxidation of phenol that is present in SSW [21]. Benzoquinone has been previously detected as an intermediate in the oxidation of phenol using Fenton's reagent [32], CWO [33] and CWPO [34]. From Fig. 9 it can be seen however that the colour of the SSW decreased significantly in the latter stages of the test, with the SSW becoming clear after approximately 60 min.





Fig. 9. Colour change during WPO of SSW. Samples from left to right- 0, 5, 10, 18, 28, 43, 60, 75, 90 min). Conditions:  $pH_i = 3.5$ , total  $H_2O_2$  added = 51 g/L (6 equal additions at 0,7,12, 20, 30 and 45 min),  $t = 90$  min,  $T = 150^\circ C$ .

### 3.2.5. Odour

Although no quantitative measurements were undertaken on the odour of SSW before and after treatment it was quite noticeable that there was no significant odour emanating from SSW that had been treated using WPO. This was in contrast to SSW treated by  $Cu(NO_3)_2$  catalysed WO which had a strong, pungent odour.

## 4. Conclusions

$Cu(NO_3)_2$  catalysed WO and WPO are both effective processes for removing TOC from SSW. A higher amount of TOC can be removed using the WPO process at lower reaction temperatures and reaction times with >80% TOC removal being achieved after 1.5 h at  $150^\circ C$  as opposed to >70% TOC removal after 3 h at  $200^\circ C$  using  $Cu(NO_3)_2$  catalysed WO.

$Cu(NO_3)_2$  catalysed WO of SSW involves free radical reactions based on the observed effects of an inhibitor (t-butanol) and the type of reaction vessel on TOC removal. Very high TOC removal from SSW (~31% after 2 h at  $200^\circ C$ ) was also observed to occur in the absence of oxygen. Based on the colour changes observed in the oxygen free system which supported a change of copper oxidation state from +2 to +1 during testing TOC removal was proposed to be most likely due to copper catalysed decarboxylation. WPO of SSW was predominantly due to oxidation by hydroxyl radicals. A minor amount of the TOC removal that occurred in the WPO tests was also most likely due to oxygen produced from degradation of hydrogen peroxide. The method used to add  $H_2O_2$  had a significant effect on TOC removal, with greater TOC removal being achieved when a number of small doses were used as opposed to one large dose.

WPO oxidation was an effective process for removing odour from SSW (no noticeable odour after treatment) as opposed to the  $Cu(NO_3)_2$  catalysed WO process where the treated SSW had a strong, pungent odour.

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