

# Applied Mineralogy

## Developments in Science and Technology

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Volume 1



International Council for Applied Mineralogy do Brasil, ICAM-BR

*Published by ICAM-BR - International Council for Applied Mineralogy do Brasil*  
*www.appliedmin.org*  
*2004, ICAM-BR, São Paulo*  
*Printed in Brazil*

Fundação Biblioteca Nacional

ISBN 85-98656-01-1



**Applied Mineralogy: Developments in Science and Technology / ed. by  
M. Pecchio, F.R.D. Andrade, L.Z. D'Agostino, H. Kahn, L.M.  
Sant'Agostino, M.M.M.L. Tassinari – São Paulo : ICAM, 2004.  
2 v.**

**ISBN**

v.1 : 85-98656-01-1

v.2 : 85-98656-02-X

**1. Applied mineralogy 2.Advanced materials 3.Analytical instrumentation  
4.Biominerals and biomaterials 5.Ceramic, glasses and cement 6.Cultural  
heritage 7.Environmental mineralogy and health 8.Gem materials  
9.Industrial minerals 10.Mineral exploration 11.Oil reservoirs 12.Ore  
mineralogy 13.Process mineralogy I.International Council for Applied  
Mineralogy do Brasil II.t.**

**Applied Mineralogy: Developments in Science and Technology / ed. by**

# Degradation of Oxamyl by Redox-modified Smectites: Effects of pH, Layer Charge, and Extent of Fe Reduction

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**ABSTRACT:** The redox states of structural iron in clay minerals may profoundly affect the chemical fate of agrochemicals. The pesticide oxamyl can be degraded either through a redox pathway, to produce N, N-dimethyl-1-cyanoformamide (DCMF), or through a base-catalyzed hydrolysis, to produce oxamyl oxime. In a preliminary study, we found that in the presence of reduced reference clay, oxamyl degraded rapidly, completely, and exclusively to oxamyl oxime (base hydrolysis pathway). This result was surprising because the reduced smectite is presumably a strong reducing agent and a priori predicts the alternative redox pathway, yielding preferentially DCMF. The main objectives of this study were therefore to: (i) better understand the basis of the observed degradation mechanism of oxamyl in the presence of reduced smectite, and (ii) evaluate if these degradation reactions would occur in nature. The hypotheses tested were: (i) the neutralization of the Brønsted basicity of the reduced smectite precludes the hydrolysis degradation pathway and invokes the redox pathway, (ii) this degradation depends on the smectite Fe(II) content and redox cycle, and (iii) oxamyl degradation occurs in soil clays reduced under natural conditions. Results revealed that for both reference clays, which were reduced to varying degrees at circum-neutral pH, oxamyl actually degrades to oxamyl oxime. As the pH of the oxamyl solution decreases, however, the Brønsted basicity of the clay surface becomes increasingly neutral, yielding preferentially DCMF. At pH 2.5, DCMF was the only observable product. Reoxidation of the smectites restores some but not all of the original clay properties.

## 1 INTRODUCTION

The swelling nature of smectite clays permits H<sub>2</sub>O and other molecules to be accommodated in the interlayer space, where numerous chemical processes may occur, including the induced transformation of organic compounds. These molecules experience short- and long-range interactions at the clay-water interface that may determine their chemical fate. The oxidation state of structural Fe in smectite is known to profoundly influence its surface interfacial properties (Stucki 1997), which, in turn, affects the clay's interactions with organic compounds. Specifically, the effective surface acidity is dramatically altered when structural Fe(III) is reduced to Fe(II). Cervini-Silva et al. (2000) showed that pentachloroethane is transformed to tetrachloroethene through the reduced clay surfaces that act as a Brønsted base.

Oxamyl is a pesticide that degrades via a hydrolytic mechanism, or via an electron transfer process. Since reduction of structural Fe in smectite alters both the surface acidity and reduction potential, which of these two pathways is favored under low- vs. high-pH conditions is unclear.

The objectives of this work were (i) to correlate

pH changes and redox state of smectite with oxamyl degradation; (ii) to determine the effect of different initial pH of oxamyl on degradation products; (iii) to evaluate the relative importance of different oxamyl:smectite ratios, and (iv) to identify any different behavior between low- and high-Fe smectites on these oxamyl degradation reactions.

Since the reduced smectite surfaces possess an elevated Brønsted basicity as well as an increased reduction potential, the question is which of these, i.e., base-catalyzed hydrolysis or reductive transformation, dominates the main chemical pathway governing the oxamyl degradation.

## 2 MATERIALS AND METHODS

Two smectite samples were used in this study: (i) Wyoming montmorillonite (sample labeled Upton, similar to API #25, Na<sub>0.72</sub>(Si<sub>7.82</sub>Al<sub>0.18</sub>)(Al<sub>3.06</sub>Fe<sup>3+</sup><sub>0.30</sub>Fe<sup>2+</sup><sub>0.02</sub>Mg<sub>0.65</sub>)O<sub>20</sub>(OH)<sub>4</sub>; Low 1980) obtained from American Colloid Company, Arlington Heights, Illinois, USA (same sample used by Yan et al. 1996), and (ii) ferruginous smectite from Grant County, Washington, USA, (sample labeled SWa-1, Na<sub>0.87</sub>(Si<sub>7.38</sub>Al<sub>0.62</sub>)(Al<sub>1.08</sub>Fe<sup>3+</sup><sub>2.67</sub>Fe<sup>2+</sup><sub>0.01</sub>Mg<sub>0.23</sub>)O<sub>20</sub>(OH)<sub>4</sub>; Manceau et al. 2000), purchased from the

Source Clays Repository of The Clay Minerals Society.

Oxidized smectites were prepared by suspending portions of the Na-saturated, freeze-dried stock material in 5 mmol L<sup>-1</sup> NaCl solution. Reduced forms of the clays were prepared by a procedure described by Stucki et al. (1984). Reoxidized forms were obtained by flowing oxygen gas for 24 hours at room temperature through the reduced clay suspension, after removing the reducing agent by centrifuge-washing three times with 5 mmol L<sup>-1</sup> NaCl solution. The amounts of Fe(II) and total structural Fe were determined by the analytical method of Komadel & Stuchi 1988.

The oxamyl solution was prepared by dissolving oxamyl powder either in acid solution, so as to obtain a final solution concentration of 25 mg L<sup>-1</sup>, at pH 3.5, or in deionized water to the same final concentration, except at pH ≈ 7.0.

Thirty mL of oxamyl:smectite suspension in a ratio of 37.5 µg : 1 g was reacted overnight in a capped teflon vessel, placed horizontally in a reciprocal shaker. A 1-mL aliquot of a 25 ppm CaCl<sub>2</sub> solution was then added to each sample, and centrifuged at 6000 rpm for 10 minutes in an IEC Clinical Centrifuge model Sorvall RC 5C Plus. The supernatant was collected and submitted to HPLC analysis and pH determination. The chemical composition of the oxamyl samples and their degradation products were determined by reverse-phase HPLC (Perkin Elmer 250 Binary LC Pump) with UV detection at 233 nm, an Alltech C18 (5 µm, 250 mm X 4.6 mm) column, and an isocratic mobile phase of 5 mmol L<sup>-1</sup> acetic acid:acetonitrile (85:15 v/v), at a flow rate of 1 mL min<sup>-1</sup>. The retention times of oxamyl, oxamyl oxime, and DCMF were identified by comparing HPLC profiles with authentic standards and by photodiode array spectroscopy (Groton PF1 Diode Array Detector System). Concentration values in samples were determined from a standard curve.

### 3 RESULTS AND DISCUSSION

Levels of structural Fe(II) obtained by dithionite reduction, as determined by the Komadel & Stucki (1988) procedure for SWa-1 and Upton clays, were over 90 mass% (relative to the total Fe) and 80 mass%, respectively. Reoxidation decreased the Fe(II) content to 10 mass% and 42 mass%, respectively.

Reduction of structural Fe greatly affects the physical and chemical properties of clays, increasing their tendency to aggregate. Previous studies also found changes in the surface area, layer charge, cation exchange capacity, swelling pressure, and color, following chemical reduction of structural Fe (Stucki et al. 1988). For SWa-1 clay, color changed

from yellow, in the oxidized form, to blue-gray in the dithionite-reduced form, and back to yellow in the reoxidized form. For Upton, color was unchanged by variations in oxidation state of the structural iron.

The rate and extend to which the oxamyl disappears in the presence of dithionite-reduced smectites were greater than in the presence of the oxidized clays. The higher the structural Fe(II) content, the lower the final concentration of oxamyl in solution (Fig. 1).

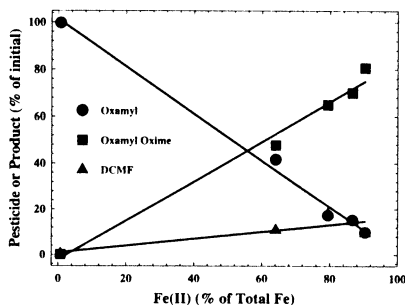


Figure 1. Degradation products of oxamyl as a function of structural Fe(II) in SWa-1.

The major degradation product in all cases, however, was the hydrolysis product, oxamyl oxime, rather than the reduction product, DCMF. These results are consistent with the hypothesis that the smectite basal surface enhances Brønsted base catalysis. The surface catalyzed reaction might, however, be mediated through the bulk water. Strong interaction with water molecules occurs at the smectite basal surface through Si-O and H-O-H coupling, which is further strengthened by reduction of structural Fe (Yan & Stucki 2000). This interaction polarizes the interlayer water toward the Si-O basal group, and makes Fe(II)-bearing smectite a strong nucleophilic reactant that accelerates the hydrolysis. Organic compounds may then interact with the basal surface through the polarized water (Cervini-Silva et al. 2000, 2001).

Despite the main interaction between smectite and oxamyl following the base-catalyzed hydrolysis pathway for both the oxidized and reduced iron states, a small amount of reductive degradation product, DCMF, was observed in dithionite-reduced smectite. The rate of DCMF production, however, was lesser than that following the hydrolysis pathway.

The pH of the oxamyl solution and the equilibrium pH of the 37.5 µg : 1 mg oxamyl: smectite oxidized, reduced, or reoxidized SWa-1 suspension were measured. Results revealed several interesting effects (Tab.1): i) the reaction with oxamyl reoxidizes some of the structural Fe(II); ii)

reoxidation with oxygen gas was incomplete; iii) pH increases with increasing Fe(II) content; iv) reduced clay buffers the solution pH to 7-9, depending on the initial pH.

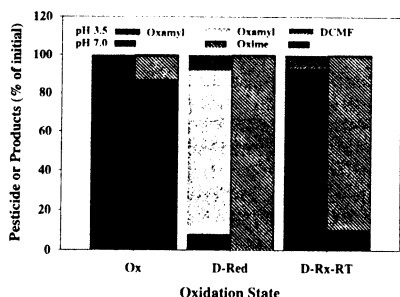


Figure 2. Degradation products of oxamyl as a function of structural Fe(II) in SWa-1.

Table 1. Changes in the oxamyl:smectite SWa-1 suspension pH and structural Fe(II) before and after oxamyl application.

	Solution pH			Fe(II)/%		
	Ox	D-Red	D-Rx-RT	Ox	D-Red	D-Rx-RT
No oxamyl	6.9	8.4	8.4/9.2	0.67	90.34	10.15
Oxamyl pH = 3.5	3.4	7.1	3.9	0.00	39.57	2.35
Oxamyl pH = 7.0	6.6	9.0	6.9	0.47	65.57	6.45

### 3.1 Oxidized smectite SWa-1

Adding oxamyl solution at pH  $\approx$  3.5 to oxidized SWa-1 in suspension decreased the pH to 3.4. At this point, no oxamyl was decomposed by the hydrolysis pathway and the clay had no Fe(II) to promote degradation by the reduction pathway (Fig.2). Addition of oxamyl solution at pH  $\approx$  7 to the suspension decreased the pH only slightly (to 6.6) and degraded oxamyl by the hydrolysis pathway. In this case, the Fe(II) content in the clay decreased slightly after reaction with oxamyl.

### 3.2 Reduced smectite SWa-1

For the reduced SWa-1, adding oxamyl solution at pH  $\approx$  7 decreased the resulting pH to 7.1 from the initial pH of 8.4 in the reduced smectite, but increased relative to the pH  $\approx$  3.5 of the oxamyl solution. Figure 2 indicates the high amount of oxamyl oxime rather than DCMF formed by oxamyl reaction with the reduced clay. Iron(II) in reduced clay favored initially the reduction pathway, decreasing the oxamyl content from 90 to  $\sim$ 40 mass%. However, if the initial pH of the suspension was increased, the hydrolysis product

was favored. When oxamyl solution at pH  $\approx$  7 was added to the reduced clay, the pH of the final suspension increased to 9.0, and oxamyl was decomposed exclusively by the hydrolysis pathway.

Contrary to observations from the oxidized and reoxidized clays, the pH in the oxamyl:smectite suspension increased relative to the added oxamyl solution when it was in contact with reduced clay.

In all conditions studied, the structural Fe(II) content decreased after reaction with oxamyl solution. However, the greatest decrease in Fe(II) was observed after the application of oxamyl solution at pH  $\approx$  3.5. At this pH, but not at pH  $\approx$  7, DCMF was preferentially produced.

### 3.3 Reoxidized smectite SWa-1

With the reoxidized clay, the degradation of oxamyl produced a small amount of DCMF, which was attributed to the remaining Fe(II) in the reoxidized clay. Although the initial pH of the clay was high, 9.2, adding oxamyl solution at pH  $\approx$  3.5 led to a decrease of the final pH  $\approx$  3.9, disfavoring degradation by the hydrolysis pathway. Fe(II) content in the clay decreased from 10 to about 2 mass% by reacting with oxamyl, which confirms the Fe(II) consumption in this reaction. By adding oxamyl solution at pH  $\approx$  7, the final pH of the suspension decreased from  $\approx$  9.9 to  $\approx$  6.9 and higher amounts of oxamyl oxime were produced. In this case, no DCMF was detected and the iron consumption was lesser (about 3.5mass%) than when oxamyl solution at pH  $\approx$  3.5 was applied (about 7.5 mass%).

### 3.4 Upton versus SWa-1

Upton clay showed the same general behavior as observed for SWa-1. However, taking into account its lower total iron content, some specific characteristics were observed for this clay. Upton oxidized and reoxidized clays have a similar behavior to the oxidized and reoxidized SWa-1, respectively (Tab. 2). Figure 3 indicates the formation of a small quantity of DCMF in oxidized clay at both pHs studied. Compared to oxidized SWa-1, oxidized Upton has more structural Fe(II), which explains degradation through the reduction pathway, producing DCMF.

Results obtained with the reduced Upton must be understood also on the basis of its relatively lower total iron content, i.e. only 3 mass% (in SWa-1 total iron content is about 16 mass%). After adding oxamyl solution at pH  $\approx$  3.5 to the reduced Upton, the pH of the resulting suspension decreased four units, compared to the initial pH of the clay; and the final pH is closer to that of the original oxamyl solution. In the same conditions, the pH for the final suspension decreased by only one unit for the

reduced SWa-1. Regarding oxamyl degradation, contrary to observations from reduced SWa-1, only DCMF was produced at pH ≈ 3.5. Only the hydrolytic degradation product was observed by adding the oxamyl solution at pH ≈ 7 to the reduced Upton. Regarding the Fe(II) consumption in the reduced Upton during the oxamyl degradation process at pH ≈ 3.5, the behavior was opposite to that observed for SWa-1 clay. The correlation between these two clays indicated that hydrolysis and reduction pathways did not occur separately; but, instead, they were closely interrelated during oxamyl degradation.

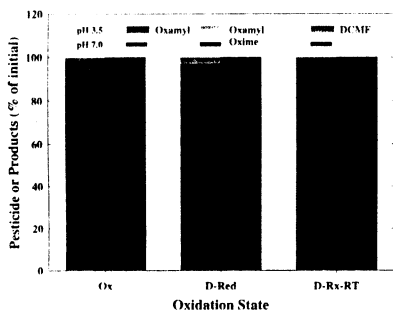


Figure 3. Degradation products of oxamyl as a function of structural Fe(II) in Upton.

Table 2. Changes in the oxamyl:smectite Upton suspension pH and structural Fe(II) before and after oxamyl application.

	Solution pH			Fe(II)/%		
	Ox	D-Red	D-Rx-RT	Ox	D-Red	D-Rx-RT
No oxamyl	7.2	8.7	8.7/9.9	12.94	80.37	42.22
Oxamyl pH = 3.5	3.8	4.5	3.8	3.64	51.19	20.17
Oxamyl pH = 7.0	6.9	8.2	7.1	9.16	27.67	21.63

#### 4 CONCLUSIONS

Iron redox reactions on clay mineral surfaces play an important role on the degradation of agrochemicals. Oxamyl can be degraded through two different mechanisms. In the hydrolysis pathway, oxamyl oxime was the most important product and in the reduction one, N, N-dimethyl-1-cyanofornamide (DCMF) was mainly produced. In the presence of reduced SWa-1 clay, hydrolysis and reduction products were found. Oxamyl oxime was always produced in higher quantity. In the presence of oxidized or reoxidized clays, only oxamyl oxime was detected. The rate at which oxamyl disappears was higher for reduced than for oxidized smectites. The surface basicity of the interlayer interface was

the major cause for the hydrolysis and the presence of structural Fe(II) was primarily responsible for the reduction reaction of the oxamyl.

The reaction to which the redox reactions take place depends upon the structural iron content, in tetrahedral sites of the clay structure and also upon the acidity of the oxamyl solution. At room temperature and circum-neutral pH, even the oxidized clay decomposed the studied agrochemical. However, a more important effect was observed with the reduced clay, which shows more effective degradation either at circum-neutral or at lowers pH, where the oxamyl solution tends to be more stable.

Reduced smectites can promote the degradation of the oxamyl in simultaneously both pathways. At lower pH, the predominant product is DCMF whereas at higher pH, the oxamyl oxime is the main product.

#### 5 ACKNOWLEDGMENTS

FRR, JWS, and JDF acknowledge financial support from the National Science Foundation, Grant N° EAR 01-26308; PK acknowledges the J.W.Fulbright Commission for fellowship support.

#### 6 REFERENCES

- Cervini-Silva, J., Larson, R. A., Wu, J., Stucki, J. W. 2001. Transformation of chlorinated aliphatic compounds by ferruginous smectite. *Environ. Sci. Tech.*, 35: 805-809.
- Cervini-Silva, J., Wu, J., Stucki, J. W., Larson, R. A. 2000. Adsorption kinetics of pentachloroethane in iron-bearing smectites. *Clays and Clay Min.*, 48: 132-138.
- Komadell, P. & Stucki, J. W. 1988. Quantitative assay of minerals for Fe(II) and Fe(III) using 1, 10-phenanthroline: *Clays and Clay Min.*, 36: 379-381.
- Low, P. F. 1980. The swelling of clay. II. Montmorillonites. *Soil Sci. Soc. Am. J.*, 44: 667-676.
- Manceau A., Lanson, B., Drits, V. A., Chateigner, D., Gates, W. P., Wu, J., Huo, D., Stucki, J. W. 2000. Oxidation-reduction mechanism of iron in dioctahedral smectites. *Am. Miner.*, 85: 133-152.
- Stucki, J. W. 1997. Redox processes in smectites: Soil environmental significance. Auerswald, K. and Stanjek, H. eds., *Advances in GeoEcology*, 30. Catena-Verlag: Amsterdam. 395-406.
- Stucki, J. W., Golden, D. C., Roth, C. B. 1984. The preparation and handling of dithionite-reduced smectite suspensions. *Clays and Clay Min.*, 32: 191-197.
- Stucki, J. W., Goodman, B. A., Schwertmann, U. 1988. eds., Iron in soils and clay minerals, D. Reidel: Dordrecht, The Netherlands.
- Yan, L., Low, P. F., Roth, C. B. 1996. Swelling pressure of montmorillonite layers versus H-O-H bending frequency of the interlayer water. *Clays and Clay Min.*, 44:749-765.
- Yan, L. & Stucki, J. W. 2000. Structural perturbations in the solid-water interface of redox transformed nontronite. *Journal of Colloid and Interface Science*, 225:429-439.