

Evaluation of corrosion action of fire fighting retardants

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Abstract

Fire fighting retardants are rapidly gaining acceptance as effective and efficient tools by fire management agencies. Nevertheless, fire operators were alarmed by a blue layer developed on aluminum surface after the use of fire-retardants while few papers considered the corrosion effect of these products. The aim of this paper is to evaluate the corrosion behaviour of aluminium and steel alloys in contact with long term fire retardants (Fire Trol[®] 931 and Fire Trol[®] 936). New tests are carried out like electrochemical measurements to obtain accurate information regarding the corrosion rate of the materials within a short period of time. The aggressiveness is found to be dependant of the solution used: in Fire Trol[®] 931 aluminium alloys showed better corrosion resistance than steel. On the contrary steel showed lower corrosion current in Trol[®] 936 in particular at beginning time of immersion. In both cases, the anodic reaction of corrosion phenomenon favours the deposition of a Prussian blue layer on the surface. This layer reduces the corrosion phenomenon on both aluminium and steel alloys.

Introduction

Fire fighting retardants and foams are rapidly gaining acceptance as effective and efficient tools by fire management agencies (Adams and others 1999).

In the United States, the yearly average Long-term fire retardants (LTR) consumption has been 15000 t of liquid concentrate equivalent over the last years. In Canada, about 6000 t of liquid concentrate are delivered each year. France (1500 t/year), Spain (300 t/year), Tunisia (50 t/year), Turkey (100 t/year), and Israel (100 t/year) are the main users of LTR products in Western Europe and in the Mediterranean countries (Angeler and others 2004).

Two types of chemicals are basically used in wildland fire control: long-term and non-foam fire retardant chemicals and short-term foam fire suppressant chemicals (McDonald and others 1996).

Long-term retardants are the liquids dropped from the airtankers or tank-tracks, often seen in media coverage of wildland fire-fighting activities. These products are supplied as either wet or dry concentrates, and are mixed with water to ensure uniform dispersal before they are dropped on the target area. When the water has completely evaporated, the remaining chemical residue forms a firebreak that retards vegetation or other materials from igniting (USDA 2004).

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Long-term fire retardants are effective fertilizers, composed of ammonium phosphate and ammonium sulphate salts (Angeler and others 2004). Long-term retardants, mixed for delivery to the fire, contain about 85% water, 10% fertilizer, and 5% other ingredients such as thickeners made of natural gum and attapulgitic clay thickener (hydrated magnesium silicate), corrosion inhibitors such as sodium dichromate or sodium fluorosilicate and bactericides (Boulton and others 2003, Hutchins and others 1989, McDonald and others 1996). Small quantities of colouring agents such as iron oxide are added to mark the location of retardant drops (McDonald and others 1996). Several papers consider the study of the toxicity and environmental stability of fire retardants considering vegetation, terrestrial fauna, fish, aquatic invertebrates and algae (Adams and others 1999, Angeler and others 2004, Boulton and others 2003, Gimenez and others 2004, Hamilton and others 1998, McDonald and others 1995, McDonald and others 1996, U.S. Forest Service 2002). Other studies evaluate effects on people's health who might be exposed to them (Gimenez and others 2004, Kalabokidis and others 2000, Lioudakis and others 2002).

Finally, the corrosive effect of fire-retardant is not studied more extensively (Gimenez and others 2004). Concentrated fire retardant solutions are highly corrosive, and often contain corrosion inhibitors (McDonald and others 1996). In fact in some cases the fire retardant substances may cause an excessive corrosion on the materials of plant tanks, air-tankers and helicopters (Palm and others 2000). Blue layers formed on aluminium surface alarmed the fire-operators.

A more complete study about corrosion problems is made by USDA (United States Department of Agriculture Forest Service) (Johnson and others 1990). In these documents corrosion tests were performed on several wildland fire chemicals. Immersion test of metals in the fire retardants are carried out for long time (90 days). The corrosion damage is evaluated through optical observation and weight difference before and after immersion. Another more exhaustive paper about this aspect is by G.A. Gehring and C.W. George (Gehring and others 1986). The authors confirmed the possibility to observe corrosion phenomena in the use of fire retardants. Different corrosion typologies are shown, including uniform corrosion and several types of localised corrosion including a guide to control the corrosion phenomena using fire retardants.

Nevertheless, this testing procedure presents some negative aspects, like a very long test time and a more effective and useful methodology is desirable. Moreover, the evaluation of corrosion effect of solutions on metal using weight difference can only be applied in the case of uniform corrosion. When localised corrosion phenomena are developed, like pitting of galvanic coupling, the application of this test method produces not-correct evaluations.

Since 40 years, new researches in corrosion field have been developed and lead to some new useful techniques. In particular the electrochemical tests in direct current (monitoring of corrosion potential, polarisation curves) and in alternate current (electrochemical impedance spectroscopy) represent today a very good method to evaluate the corrosion behaviour of materials (ASTM 1989a, 1989b, 1997, Fontana and others 1986, Revie 2000, Trethewey and others 1988). These tests allow to obtain accurate information regarding the corrosion rate of the materials within a short period of time. They offer a high reproducibility and for these reasons they are still more frequently used both in research studies and in industrial laboratories.

One of the most used LTR are Fire Trol[®] 931 and Fire Trol[®] 936 produced by Chemonics Industries (Canada) and in Europe by Biogema (France). Fire Trol[®] 931 is a liquid concentrate fire retardant designed to be diluted with water and used for aerial application to control wildfire (USDA 2004). It is a concentrate mixture of

ammonium polyphosphate (80% to 95%), sodium hexacyanoferrate (0.1% to 3%) iron oxide (0.1% to 3%, which provides the colour) and a minor amount of a clay thickener like attapulgite to suspend the colour and enhance visibility. Actual amounts of each ingredient may vary from time to time (USDA 2004, Palm and others 2000). The mix of LTR with water is usually pumped directly into aircrafts. Fire Trol[®] 936 is very similar to Fire Trol[®] 931. It consists in a purple liquid with biodegradable dye and it is used mixed with water to drop from tank-tracks (Firetrolcanada 2007).

The aim of this paper is then to assess the corrosion behaviour of aluminium alloys and steel in contact with Fire Trol[®]931 and Fire Trol[®] 936 using electrochemical measures.

Experimental

Discs with 1 cm² surface made of aluminium alloy 2024 (4% Cu, 0.6% Mg, 0.7% Mn, 0.7% Fe, 0.5% Si, Al bal.) and carbon steel (0.1%C, Fe bal.) are used. The sample surfaces are polished with an emery paper (800 mesh) and then degreased with acetone using ultrasonic bath before testing.

LTR Fire Trol[®] 931 and Fire Trol[®] 936 manufactured by Biogema (France) are tested. The test solutions are produced by the mix 20% of LTR in tap water (Marseille – France).

Electrochemical tests are carried out to obtain information about the corrosion behaviour of these metals and about the aggressiveness of the fire retardant liquids. The three electrodes electrochemical cell is used with a SCE (+242 mV SHE) reference electrode and a platinum grid as counter-electrode. An EG&G 273 potentiostat connected to a FRA Solartron 1260 and a PC are used. Potentiodynamic polarization tests are performed using a polarization rate of 0.5 mV/s, starting from cathodic potentials. Electrochemical Impedance Spectroscopy (EIS) measurements are carried out with a signal amplitude of 10 mV, in the frequency range of 100 kHz to 10 mHz at free corrosion potential. The impedance data are fitted using Zplot software to obtain the values of the electrical parameters like the polarization resistance. The total testing time is 24 hours, with a measurement per each hour. After 2 and 24 hours of immersion, the sample surfaces are analysed using optical and environmental scanning electron microscopes (TMP ESEM FEI).

Results and discussion

Figure 1 shows the polarization curves of aluminium alloy and steel in solutions made with Fire Trol[®] 931 and Fire Trol[®] 936. This test allows to obtain very useful information about the corrosion behaviour of the materials (Fontana and others 1986, Revie 2000).

Aluminium alloy samples present always the same trend in both solutions showing a very low anodic current density, lower than $4 \cdot 10^{-4}$ A/cm², indicating a low reactivity of this material. The anodic current increases with the potential applied and no passive behaviour is observed.

Steel sample curves show a different trend. It is possible to observe in Fire Trol[®] 931 solution a passivation phenomenon. The formation of this protective layer arises after an attack of the surface, which is correlated with an increase of the anodic current following by a decrease. Considering this behaviour it is possible to affirm

that the passive phenomenon is not direct, but implies the passage by a corrosion of the surface.

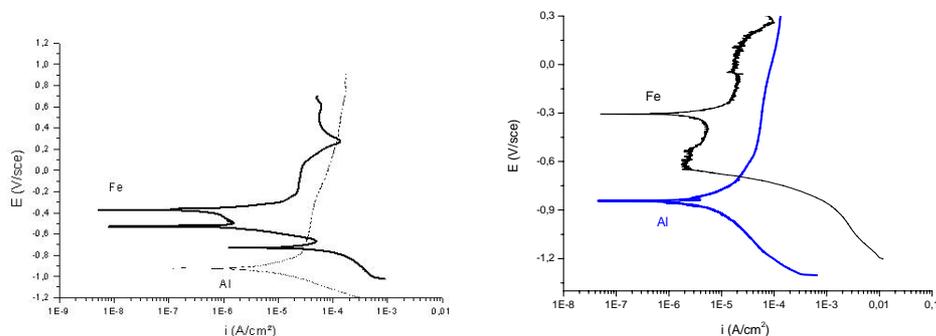


Figure 1 - Potentiodynamic curves of aluminium alloy and steel using Fire Trol® 931 solution (on the left) and Fire Trol® 936 solution (on the right).

This passive behaviour could also be observed in the Fire Trol® 936 solution. In this case we do not observe the active-passive transition. Probably the surface passivation is more quickly. The nobler corrosion potential confirms this affirmation.

After these polarization tests a blue film is present on all surfaces.

More precise information can be obtained by EIS measurements. This electrochemical test is a not destructive technique which permits to follow the behaviour of samples during immersion. The interest of the electrochemical impedance tests is to evaluate the corrosion behaviour of different metals with minimal perturbations (Macdonald 1987, Scully 1993). This fact is useful to evaluate the change of corrosion rate during immersion time and to highlight the formation of the blue layer on the sample surface.

As example, figure 2 shows the EIS diagrams (Nyquist representation) of the aluminium alloys in Fire Trol® 936 solution in function of immersion time. It is possible to observe an increase of impedance values during the first immersion hours. After 13 hours of immersion, a practically constant behaviour is observed. This fact could be related to the formation of a constant thickness layer on the surface. The formation of this layer is correlated to the presence of a starting part of a second loop, at lower frequencies (on the right in the diagrams).

By fitting the data, it is possible to quantify the corrosion phenomenon. In fact, the extrapolation at low frequency of the impedance plot and the intersection with the Z real impedance axis allow to obtain the total resistance (R_{tot}). In the first approximation the total resistance is inversely proportional to the corrosion rate (Macdonald 1987, Scully 1993). Higher are the R_{tot} values lower is the corrosion rate of the material.

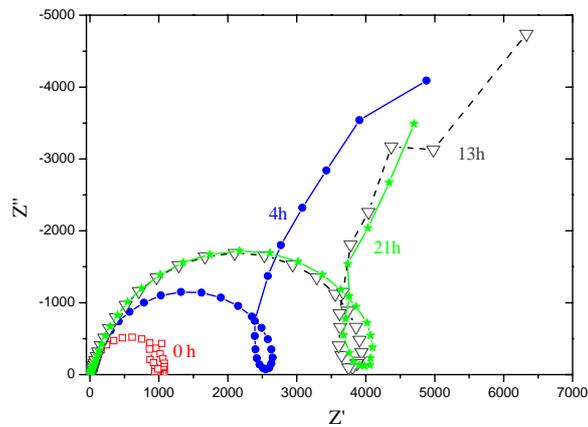


Figure 2 - EIS diagrams (Nyquist representation) of the aluminium alloys in Fire Trol[®] 936 solution if function of immersion time (0, 4, 13 and 21 hours).

Figure 3 shows the R_{tot} trend of the aluminium alloy and steel in both studied solutions. It is possible to observe a different behaviour of the material in function of the tested solutions.

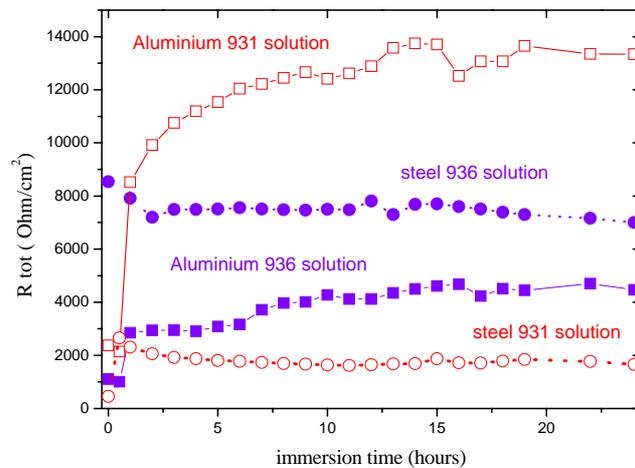


Figure 3 - R_{tot} trend of the aluminium alloy and steel in Fire Trol[®] 931 solution (empty points -red curves) and Fire Trol[®] 936 solution (filled points -violet curves).

Considering the behaviour in Fire Trol[®] 931, we can say that aluminium shows a low corrosion rate. After the first immersion time a quickly increase of R_{tot} is evident with a reduction of corrosion rate. On the contrary, steel shows lower R_{tot} values, indicating a higher corrosion rate. In addition the R_{tot} values remain constant during immersion indicating no change neither in corrosion rate nor on the surface. This is in good accordance with the previous direct current results: the blue deposit forms with difficulty and is probably not very protective.

A different behaviour is observed in Fire Trol[®] 936 solution. With respect to the previous solution, the aluminium alloy shows lower R_{tot} values indicating a more

active process. The values increase very slowly indicating the lower reduction of corrosion rate. Probably the deposit which forms on the surface is less protective due to the limited thickness or to the presence of porosities and defects. On the contrary, the steel shows higher R_{tot} values than aluminium in the same solution and than steel in Fire Trol[®] 931, without any increase of the values with the immersion time.

Using the value of R_{tot} it is possible to calculate the corrosion rate of the metals ASTM 1989a, Fontana and others 1986), using the following approximated equation:

$$i_{cor} = \frac{0.0175}{R_{tot}}$$

Table 1 reports the corrosion currents of both studied materials in Fire Trol[®] 931 and Fire Trol[®] 936 solutions.

		Total resistance (Ωcm^2)		Corrosion current ($\mu\text{A}\cdot\text{cm}^{-2}$)	
		0 h	24 h	0 h	24 h
Aluminium alloy	Fire Trol [®] 931	2376	13340	7.4	1.3
	Fire Trol [®] 936	1108	4461	15.8	3.9
Steel	Fire Trol [®] 931	459	1661	38	10.6
	Fire Trol [®] 936	8539	7167	2	2.9

Table 1 -Values obtained by fitting the impedance data and calculated corrosion current of materials in Fire Trol[®] 931 and Fire Trol[®] 936 solutions.

From these values it is clear that aluminium shows a low corrosion rate in Fire Trol[®] 931 solution. On the contrary in Fire Trol[®] 936 solution, steel shows the lower corrosion rate. Nevertheless in all case these values remain low.

It is possible to observe that in all cases, the corrosion current decreases during immersion due to the formation of a protective layer. This deposit shows a protective character against corrosion.

In all cases after 24 hours it is possible to observe the presence of a blue deposit on the samples surface (fig.4). Nevertheless in particular on steel immersed in Fire Trol[®] 931 solution, the deposit appears less compact and not very thick.

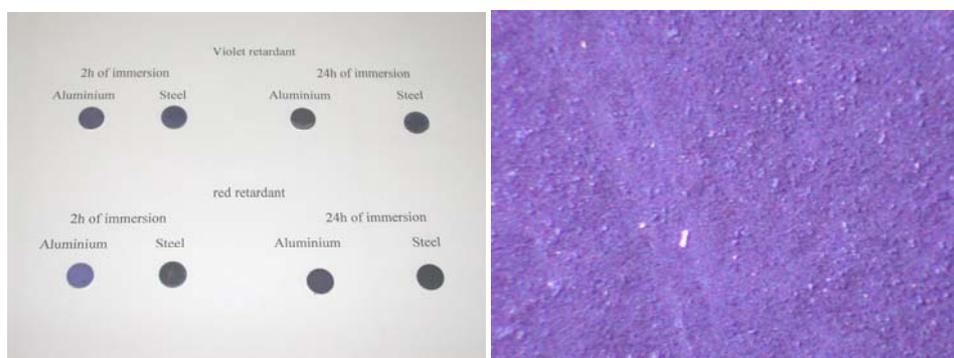


Figure 4 - samples surface after 2 and 24 hours of immersion in Fire Trol[®] 931 and Fire Trol[®] 936 solutions (on the left); deposit present on aluminium surface after 24h of immersion in Fire Trol[®] 936 solution (on the right).

Extended morphological informations and chemical analysis are carried out using EDXS (Energy Dispersion X-ray Spectroscopy) coupled with an ESEM. Figure 5 shows the deposit formed on the aluminium surface after 24h of immersion in both solutions. In both cases it is possible to observe the presence of a layer made with cubic crystals. A second structure with a stick form is also present. The layer produced during immersion in the purple Fire Trol[®] 936 solution shows several little defects as clearly observable on figure 5 (picture on the right).

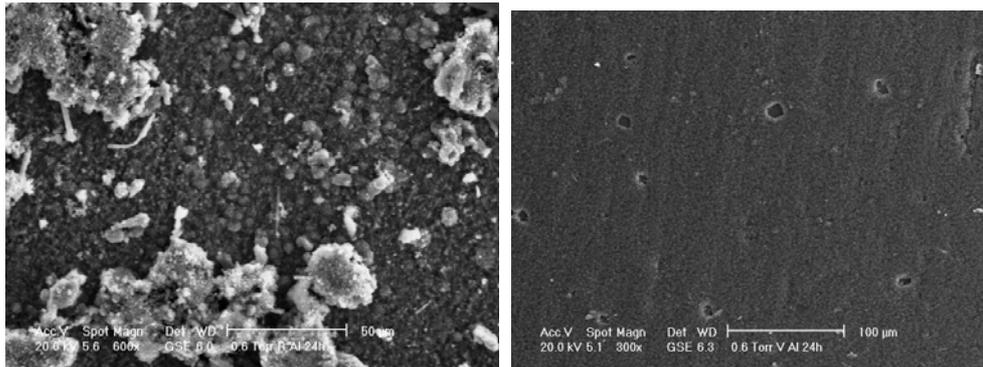


Figure 5 - deposits present on the aluminium surface after 24 hours of immersion in Fire Trol[®] 931 (on the left) and Fire Trol[®] 936 solutions (on the right).

The EDXS analysis made on the stick structures shows the presence of Fe and P. These structures are probably related to phosphates. On the cubic structure, the signals of Fe, C and N increase remarkably probably due to the presence of compound made by iron and cyanic groups. Analysis made on the defects of deposits, obtained from the purple solution, highlights the presence of aluminium indicating that, in this area, the substrate is uncovered (fig.6). The presence of these defects could justify the lower R_{tot} values, indicating a higher corrosion rate.

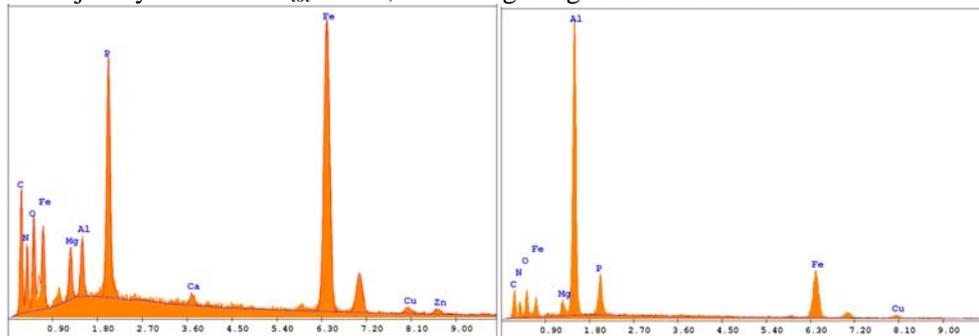


Figure 6 - EDXS spectra carried out on cubic structures (on the left) and in correspondence of defects (on the right) observed on aluminium surface.

Considering the deposits formed on steel surface it is possible to observe several differences in function of the solution used. In Fire Trol[®] 931, a non homogeneous deposit is formed only on few areas (fig.7). It presents some larger and regular crystallites like on aluminium surface. On these large crystal structures, the signal of P is more intense due to the probable presence of phosphate. The signals of C, N and Fe are less intense than those obtained on aluminium sample.

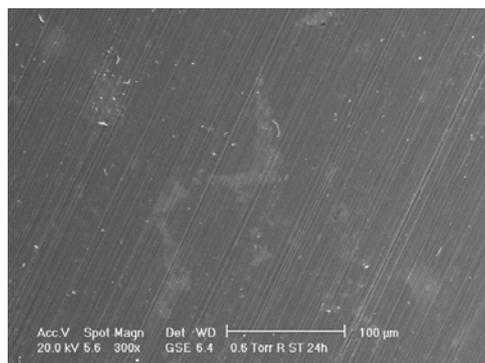


Figure 7 - deposit present on the steel surface after 24 hours of immersion in Fire Trol® 931 solution.

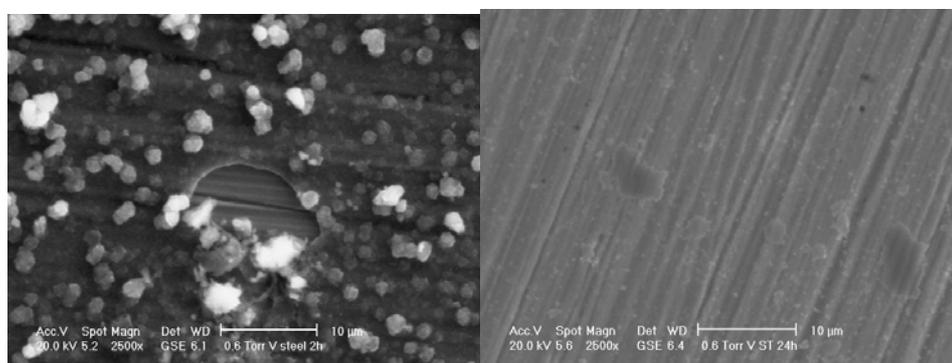


Figure 8 - deposits present on the steel surface after 2 and 24 hours of immersion in Fire Trol® 936 solution.

After immersion in the Fire Trol® 936 solution, a more evident and thick deposit is present (fig.8). A first layer is clearly visible on figure 8 (left) with a cubic structure. The nature of blue deposits is studied by XRD analysis and FT-IR analysis. Both techniques highlight the presence of iron (III) hexacyanoferrate (II), ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$), also called Prussian blue, as reported in previous papers (Rossi and others 2006a, 2006b).

No differences are observed in the nature of deposits in function of metallic substrate and in function of type of LTR.

Probably the oxidation of metals produces locally a decrease of pH, which permits the formation on the metallic surface of the Prussian Blue compound coming from the LTR constituents.

Conclusion

- Aluminium alloy and steel show a good corrosion behaviour in solutions made with tap water and Fire Trol® 931 and Fire Trol® 936.
- In the Fire Trol® 931 solution, steel is less resistant to corrosion than aluminium; on the contrary, in Fire Trol® 936 solution the aluminium alloys shows worse behaviour than steel.
- On the surfaces of these materials, a blue deposit is formed during immersion whatever the solution used. These layers are more evident on the aluminium surface.

- These layers reduces the corrosion rate of the materials, acting as a protective barrier.

References

- Adams R., Simmons D. 1999. **Ecological Effects of Fire Fighting Foams and Retardants**. In proc. of Australian Bushfire Conference, Albury, July 1999, on <http://www.csu.edu.au/special/bushfire99/papers/adams/index.htm>
- Angeler D.G., Rodriguez M., Martin S., Moreno J.M. 2004. **Assessment of application-rate dependent effects of a long-term fire retardant chemical (Fire Trol 934) on *Typha domingensis* germination**. *Environment International*. 30: 375– 381.
- ASTM standard G102-89. 1989 **Standard Practice for Calculation of corrosion rates and Related Information from Electrochemical Measurements**. American Society for Testing and Materials West Conshohocken US.
- ASTM standard G59-97. 1997. **Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements**. American Society for Testing and Materials West Conshohocken US.
- ASTM standard G3-89. 1989. **Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing**. American Society for Testing and Materials West Conshohocken US.
- Boulton A.J., Moss G.L., Smithyman D. 2003. **Short-term effects of aerially-applied fire-suppressant foams on water chemistry and macroinvertebrates in streams after natural wild-fire on Kangaroo Island, South Australia**. *Hydrobiologia*. 498: 177–189.
- Firetrolcanada 2007. <http://www.firetrolcanada.com/ft934-936.php>.
- Fontana M. G.1986, **Corrosion engineering**, 3. ed., McGraw-Hill, New York, US.
- Gehring G.A., George C.W., 1986. **Guidelines for preventing fire retardant corrosion**, General Technical Report INT 210, USDA Forest Service, Intermountain Research Station, Ogden UT, US.
- Gimenez A., Pastor E., Zarate L., Planas E., Arnaldos J. 2004. **Long-term forest fire retardant: a review of quality, effectiveness, application and environmental considerations**. *International Journal of Wildland Fire*. 13: 1-15.
- Hamilton S., Larson D., Finger S., Poulton B., Vyas N., Hill E. 1998. **Ecological effects of fire retardant chemicals and fire suppressant foams**. Jamestown, ND: Northern Prairie Wildlife Research Center on <http://www.npwrc.usgs.gov/resource/othrdata/fireweb/fireweb.htm> (Version 02MAR98).
- Hutchins B., Ramsey G.1989. **An Analysis of foam, long and short term retardants**. Roscommon Equipment Center Program Project No. 41-B; Northeast Forest Fire Supervisors, Michigan's Forest Fire Experiment Station US.
- Johnson C.W., George C.W. 1990. **Relative Corrosivity of Currently Approved Wildland Fire Chemicals**. Research paper int.437, USDA Forest Service, Intermountain Research Station, Ogden UT US.
- Kalabokidis K.D. 2000. **Effects of wildfire suppression chemicals on people and the environment – a review**. *Global Nest: the Int. J.* 2: 129-137.

- Land and Forest Service Alberta Environmental Protection 2001. **Wildfire Foam Application Manual**. Land and Forest Service Alberta Environmental Protection, Edmonton, Alberta Canada.
- Liodakis S., Bakirtzis D., Lois E., Gakis D. 2002. **The effect of $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ on the spontaneous ignition properties of *Pinus halepensis* pine needles**. Fire Safety Journal. 37: 481–494.
- Macdonald J. R. 1987. **Impedance spectroscopy :emphasizing solid materials and systems**, Wiley, New York, US.
- McDonald S.F., Hamilton S.J., Buhl K.J., Heisinger J.F 1995. **Acute Toxicity of Fire-Retardant and Foam Suppressant Chemicals to *Hyalella Azteca* (Saussure)**. Environmental Toxicology and Chemistry.16: 1370-1376 on
[www.npwr.usgs.gov/resource/othrdata/ fireweb/hyalazte/hyalazte.htm](http://www.npwr.usgs.gov/resource/othrdata/fireweb/hyalazte/hyalazte.htm) (Version 02mar98)
- McDonald S.F., Hamilton S.J., Buhl K.J., Heisinger J.F. 1996. **Acute Toxicity of Fire Control Chemicals to *Daphnia magna* (Straus) and *Selenastrum capricornutum* (Printz)**. Ecotoxicology and Environmental Safety. 33: 62–72.
- Palm S., Taylor R., Johnson C., Pfouts B., Forbes A., 2000. **Lot Acceptance, Quality Assurance, and Field Quality Control for Fire Retardant Chemicals**. National Wildfire Coordinating Group, NFES 1245 Sixth Edition—May 2000 Boise Idaho US.
- Revie R. W. 1988, **Uhlig's corrosion handbook**, Wiley New York, US.
- Rossi S., Eyraud M., Vacandio F., Massiani Y. 2006.**Corrosion behaviour of aeronautic alloys in fire sighting retardant**. in proc. Eurocorr 2006, Maastricht (Olanda), 25-28 September 2006, on CD-R.
- Rossi S., Eyraud M., Vacandio F., Massiani Y. 2006.**Corrosivity of long-term fire retardant Fire Trol[®] 931 and Fire Foam[®] 103 on aluminium alloys and steel**. sent to Materials Chemistry and Physics.
- Scully J. R. 1993. **Electrochemical impedance :analysis and interpretation**, American society for testing and materials, Philadelphia, US.
- Trethewey K. R., Chamberlain J. 1988, **Corrosion for students of science and engineering**, Longman, Harlow UK.
- USDA. 2004. **Wildland Fire Chemicals Systems** Forest Service, Missoula, MT USA, on http://www.fs.fed.us/rm/fire/wildland_chemicals.htm
- U.S. Forest Service 2002. **Environmental implication of fire-retardant chemicals**. U.S. Forest Service--June 2002.
on <http://www.cerc.cr.usgs.gov/pubs/center/pdfDocs/ECO-03.pdf>