Final Report on Leachable Metals in Scrap Tires

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Introduction.

In October 1990, the VDOT Scrap Tire Task Force requested a long term study of the leachable metals present in scrap tires. The study was started in December 1990, and an interim report covering the first six months of the study was issued in September 1991 (Ref. 1). The study has now been completed and this report presents the findings.

Scope of Study.

The original request was for a study covering time intervals from one hour to one year, at pH's of 4, 7 and 8. Analysis of 17 elements was requested; we were able to analyze for all except sulfur either in-house or using the services of an outside laboratory. In addition, a Toxicity Characteristic Leaching Potential (TCLP) study was done.

Methodology.

The methodology for the long term study was based on that used in the Twin City study (Ref. 2). Briefly, approximately 500 g samples of shredded tires were placed in one gallon polyethylene containers and incubated with 2-3 liters of extraction fluid. For the pH 4 extraction, deionized water was used and 0.5 N acetic acid was added as needed to maintain the pH between 4 and 5, until the container was full. The pH was then monitored at intervals. The pH 7 extraction was performed using a 0.9% sodium chloride solution to mimic the effect of use of road salt. In reality, the pH of this solution was close to 6, but, no attempt was made to adjust the pH. The pH 8 extraction used a 1% ammonium acetate solution adjusted to pH 8 by addition of a small amount of 0.5 N ammonium hydroxide. This solution maintained a stable pH. The containers were kept in the dark at a temperature of 70 - 80 degrees F and shaken at weekly intervals. The pH was monitored periodically. At the end of each time interval, the samples were filtered and the filtrates were digested and analyzed using the analytical methods presented in Table I. Silver was not determined in the pH 7 extract, because it contained a large excess of chloride. This caused significant matrix effects in the analysis, and in any case, it is likely that any leached silver would have been precipitated as silver chloride and removed during the filtration step.

The TCLP test was performed according to EPA 1311 (Ref. 5,6), with some minor modifications. It was not practicable to reduce the sample particle size to pass the 3/8 inch sieve, so a representative 600 g sample was used. As a consequence, it was not possible to use the twentyfold volume extraction ratio; a ratio of approximately 2.84 was used.

Results.

The results of the long term study are presented in Tables II-IV. The avg pH is the time-weighted average of actual pH measurements made during the course of the study. Results are presented as normalized values to account for differing sample weights and solution volumes. Zinc (Zn), iron (Fe), calcium (Ca), and magnesium (Mg) are presented in milligrams per kilogram (parts per million); all other elements are presented in micrograms per kilogram (parts per billion). The results are averages of duplicate samples at time intervals of up to one month, and triplicates for the longer term samples. Because of the large number of extracts generated, not all of the analyses were performed on all of the extracts. Analyses for arsenic, selenium and mercury were only performed on the final (one year) extract. The one year leaching studies were actually extended to 14.5 months for the pH 4 and 7 extractions, and 13.5 months for the pH 8 extraction.

The results of the TCLP study are presented in Table V.

Discussion.

Metals leached most readily at pH 4; this confirms previously published findings. The most abundant metal in the leachate is iron; at pH 4 it reached a saturating concentration of about 30,000 mg/kg (3%) within two weeks. Zinc was also readily leached at pH 4, reaching levels of the order of 150 mg/kg at two months. Using the "worst case scenario" (ref. 2), this would correspond to a concentration of 120 ppm within the porewater volume at the waste tire subgrade. As a point of interest, Henrico County does not allow discharge of more than 1.53 ppm zinc into its sewage treatment system.

Leaching of other elements was much less marked, particularly at higher pHs. Copper and zinc show some unusual kinetics at the higher pHs--higher concentrations being found in the leachates at one day than at six months. A possibly explanation is plating out of solubilized material on the walls of the container used in the experiment.

Two other phenomena are worth noting. At the higher pHs, particularly pH 8, a great deal of carbon black was extracted, along with some oily material. This is consistent with the Twin City findings, that organics are more readily extracted under basic conditions. Also, after about two weeks of leaching at pH 4, some gas generation was observed. At this stage of the study, the containers were full of tires plus liquid, and sufficient pressure was generated to cause bulging of the container and oozing around the lid. This may be associated with bacterial activity; the tires were often coated with soil which may contain bacteria capable of metabolizing acetate to carbon dioxide. This was tested experimentally by substituting benzoic acid (a bacterial inhibitor) for the acetic acid at the same pH. There was no gas generation in the presence of benzoic acid.

The results of the TCLP test indicate that the concentrations of metals in the leachates are well below regulatory levels, even though these leachates are seven times more concentrated than normal TCLP extracts. This is consistent with the findings of the study performed for the Rubber Manufacturers Association by Radian Corporation (Ref. 5).

Acknowledgements.

The author recognizes the contributions of the following individuals: Sam Henderson, Robert Ridley and Jim Stone for their assistance with sample digestion and analysis; Bill Bailey for thoughtful discussion in the design and interpretation of this work; Morris Menefee for provision of the shredded tire samples.

TABLE I

ANALYTICAL METHODS

Element	Method	EPA No.
Aluminum (Al)	HGA	202.2
Arsenic (As) *	HGA	7060
Barium (Ba) *	HGA	7081
Calcium (Ca)	Flame AA	7140
Cadmium (Cd)	HGA	7131
Chromium (Cr)	HGA	7191
Copper (Cu)	Flame AA	7210
Copper (Cu)	HGA	7211
Iron (Fe)	Flame AA	7380
Mercury (Hg) *	Cold vapor	7471
Magnesium (Mg)	Flame AA	7450
Nickel (Ni)	HGA	249.2
Lead (Pb)	HGA	7421
Silver (Ag) *	HGA	7761
Selenium (Se) *	HGA	7740
Zinc (Zn)	Flame AA	7950
Tin (Sn)	HGA	282.2

* Analyses performed by Environmental Laboratories Inc., Richmond, VA

TABLE II--metals leached at pH 4

Time	Avg pH	Zn mg/kg	Fe mg/kg	Ca mg/kg	Mg mg/kg
1 hour	4.10	13.2	5.3	0.8	0.4
2 hours	4.03	18.6	8.5	1.7	0.4
1 day	4.18	25.2	96.1	3.4	0.6
2 days	4.28	15.1	184.5	6.5	0.4
1 week	4.28	102.1	13992	7.9	1.2
2 weeks	4.44	112.0	31622	8.8	1.8
1 month	4.45	127.4	30668	15.1	1.5
2 months	4.67	153.7	30314	24.2	3.3
6 months	4.55	62.5	31344	18.5	3.0
1 year	4.74	124.7	18788	128.4	5.8

Time	Avg pH	Cd ug/kg	Cr ug/kg	Ni ug/kg	Pb ug/kg
1 hour	4.10	1.9	6.3	<20	<20
2 hours	4.03	2.6	<4.0	<20	<20
1 day	4.18	3.5	7.0	48.1	<20
2 days	4.28	nd	nd	nd	nd
1 week	4.28	3.5	<4.0	2116	49.2
2 weeks	4.44	nd	nd	nd	nd
1 month	4.45	<1.2	82.4	2460	<30
2 months	4.67	nd	nd	nd	nd
6 months	4.55	<1.2	12.6	647	<30
1 year	4.74	2.1	152	928	138

nd = not determined

TABLE II (continued)--metals leached at pH 4

Time	Avg pH	Cu ug/kg	Al ug/kg	Ba ug/kg	Ag ug/kg
1 hour	4.10	109	185	87	2.3
2 hours	4.03	188	321	78	2
1 day	4.18	192	23	25	1.5
2 days	4.28	nd	nd	nd	nd
1 week	4.28	328	746	422	2.5
2 weeks	4.44	nd	nd	nd	nd
1 month	4.45	13	177	1262	3.2
2 months	4.67	nd	nd	nd	nd
6 months	4.55	<12	<24	2083	5.2
1 year	4.74	159	491	1537	10

Time	Avg pH	Sn ug/kg	As ug/kg	Hg ug/kg	Se ug/kg
1 hour	4.10	<40	nd	nd	nd
2 hours	4.03	<40	nd	nd	nd
1 day	4.18	<40	nd	nd	nd
2 days	4.28	nd	nd	nd	nd
1 week	4.28	<50	nd	nd	nd
2 weeks	4.44	nd	nd	nd	nd
1 month	4.45	<60	nd	nd	nd
2 months	4.67	nd	nd	nd	nd
6 months	4.55	<60	nd	nd	nd
1 year	4.74	<60	<25	<1	<30

nd = not determined

TABLE III--metals leached at pH 7

Time	Avg pH	Zn mg/kg	Fe mg/kg	Ca mg/kg	Mg mg/kg
1 hour	5.99	6.6	11.4	1.4	0.2
2 hours	5.87	14.3	29.2	2.6	0.3
1 day	6.00	14.7	83.1	3.8	0.5
2 days	5.97	6.0	87.4	3.0	0.3
1 week	6.01	4.1	85.7	3.3	0.4
2 weeks	6.02	2.7	79.6	4.1	0.5
1 month	6.00	2.3	91.7	5.1	0.8
2 months	6.15	0.3	103	8.5	1.2
6 months	6.32	0.2	73.8	10.8	1.8
1 year	6.69	0.6	84.3	6.8	1.6

Time	Avg pH	Cd ug/kg	Cr ug/kg	Ni ug/kg	Pb ug/kg
1 hour	5.99	nd	nd	nd	nd
2 hours	5.87	nd	nd	nd	nd
1 day	6.00	27.6	5.3	138	<20
2 days	5.97	nd	nd	nd	nd
1 week	6.01	<1.0	4.6	40	nd
2 weeks	6.02	nd	nd	nd	nd
1 month	6.00	<1.0	<4.0	81	21
2 months	6.15	nd	nd	nd	nd
6 months	6.32	8.2	<4.0	31	<20
1 year	6.69	<1.0	16	35	<20

nd = not determined

TABLE III (continued)--metals leached at pH 7

Time	Avg pH	Cu ug/kg	Al ug/kg	Ba ug/kg	Ag ug/kg
1 hour	5.99	nd	nd	nd	nd
2 hours	5.87	nd	nd	nd	nd
1 day	6.00	146	<20	290	nd
2 days	5.97	nd	nd	nd	nd
1 week	6.01	15.7	269	300	nd
2 weeks	6.02	nd	nd	nd	nd
1 month	6.00	<10	79	339	nd
2 months	6.15	nd	nd	nd	nd
6 months	6.32	<10	<20	776	nd
1 year	6.69	35	213	415	nd

Time	Avg pH	Sn ug/kg	As ug/kg	Hg ug/kg	Se ug/kg
1 hour	5.99	nd	nd	nd	nd
2 hours	5.87	nd	nd	nd	nd
1 day	6.00	<40	nd	nd	nd
2 days	5.97	nd	nd	nd	nd
1 week	6.01	<40	nd	nd	nd
2 weeks	6.02	nd	nd	nd	nd
1 month	6.00	<40	nd	nd	nd
2 months	6.15	nd	nd	nd	nd
6 months	6.32	<40	nd	nd	nd
1 year	6.69	<40	<15	<0.7	<19

nd = not determined

TABLE IV--metals leached at pH 8

Time	Avg pH	Zn mg/kg	Fe mg/kg	Ca mg/kg	Mg mg/kg
1 hour	7.98	5.4	1.6	4.2	0.3
2 hours	8.00	6.8	1.3	4.5	0.4
1 day	7.97	10.5	1.4	3.9	0.4
2 days	7.92	8.4	4.9	4.1	0.7
1 week	7.80	2.2	11.5	12.5	1.1
2 weeks	7.84	0.6	131	12.7	1.8
1 month	7.81	<0.1	41.1	15.6	2.0
2 months	7.63	<0.1	134	15.3	1.9
6 months	7.63	0.2	214	16.9	2.4
1 year	7.59	0.6	75.7	21.4	3.1

Time	Avg pH	Cd ug/kg	Cr ug/kg	Ni ug/kg	Pb ug/kg
1 hour	7.98	nd	nd	nd	nd
2 hours	8.00	nd	nd	nd	nd
1 day	7.97	2.6	6.8	39.4	<20
2 days	7.92	nd	nd	nd	nd
1 week	7.80	<1.0	<4.0	94.2	<20
2 weeks	7.84	nd	nd	nd	nd
1 month	7.81	<1.0	<4.0	81.2	<20
2 months	7.63	nd	nd	nd	nd
6 months	7.63	<1.0	4.6	22.0	<20
1 year	7.59	3.3	2.1	111.3	<20

nd = not determined

TABLE IV (continued)--metals leached at pH 8

Time	Avg pH	Cu ug/kg	Al ug/kg	Ba ug/kg	Ag ug/kg
1 hour	7.98	<400 *	nd	nd	nd
2 hours	8.00	687 *	nd	nd	nd
1 day	7.97	2582 *	<20	148	61
2 days	7.92	1546 *	nd	nd	nd
1 week	7.80	759 *	1283	211	2.3
2 weeks	7.84	<400 *	nd	nd	nd
1 month	7.81	<10	271	181	2.0
2 months	7.63	nd	nd	nd	nd
6 months	7.63	<10	<20	190	2.2
1 year	7.59	21	122	1073	1.1

Time	Avg pH	Sn ug/kg	As ug/kg	Hg ug/kg	Se ug/kg
1 hour	7.98	nd	nd	nd	nd
2 hours	8.00	nd	nd	nd	nd
1 day	7.97	<40	nd	nd	nd
2 days	7.92	nd	nd	nd	nd
1 week	7.80	<40	nd	nd	nd
2 weeks	7.84	nd	nd	nd	nd
1 month	7.81	<40	nd	nd	nd
2 months	7.63	nd	nd	nd	nd
6 months	7.63	<40	nd	nd	nd
1 year	7.59	<40	<16	<0.8	<20

nd = not determined
* Cu analysis by flame

TABLE V

TCLP Metals

Element	Conc. in extract,ppb	Conc. in tires, ug/Kg
Cd	1.55	4.4
Cr	2.8	7.9
Pb	19.6	55.6
Ag	<1.0	<2.8
Ni	39.7	113
Al	148	420
Cu	83	235
Sn	<25	<71
	Conc. in extract,ppm	Conc. in tires,mg/Kg
Fe	120	341
Zn	10.6	30
Mg	0.108	0.307
Ca	1.00	2.84

References.

1. Interim Report on Scrap Tire Study by Wendy Ealding, Virginia DOT Materials Division dated September 9, 1991.

2. Waste Tires in sub-grade Road Beds by Twin City Testing Corporation, St. Paul, MN dated February 19, 1990

3. EPA SW-846 Test Methods for Evaluating Solid Waste Third Edition November 1986.

4. EPA 200 Series Methods for Chemical Analysis of Water and Wastes March 1983.

5. A Report on the RMA TCLP Assessment Project by Radian Corporation, Austin, TX dated September 25, 1989.

6. Federal Register Vol. 51 No. 114 40CFR Parts 261, 271 and 302 dated June 13, 1986 and May 24, 1989.