REFERENCE 5

QUALITY
ANALYTICAL
LABS, INC.

Job #: 7-650
Date: 4/10/91

LTV Steel
3001 Dickey Road
East Chicago, IN 46312

Attn: Mohammed Babar

Sampling Date: 4/4/91
Analyses Date: 4/4-4/10/91

Technique/Method: As per SW 846 Methods 6010,7196 and 1310

Identification: Six samples taken by Mohammed Babar identified as:

LTV STEEL
ROLL SHOPS CHROME STUDY

Results:

Sample 84" H.S.M. Roll Shop Sludge

Parameter	MDL (ppm)	Analysis (ppm)
Total Chromium	2.0	1430
Total Hexavalent Chrome	2.0	9.6

Sample 84" H.S.M. Roll Shop Water

Total Chromium	0.1	1.5
Total Hexavalent Chrome	0.1	BDL

Sample #3 S.M. Roll Shop Sludge

Total Chromium	2.0	1310
Total Hexavalent Chrome	2.0	12

Sample #3 S.M. Roll Shop Water

Total Chromium	0.1	0.3
Total Hexavalent Chrome	0.1	BDL

QUALITY
ANALYTICAL
LABS, INC.

Parameter	MDL (ppm)	Analysis (ppm)
Sample #2 T.M. Roll Shop Sludge		
Total Chromium	2.0	1110
Total Hexavalent Chrome	2.0	29
Sample #2 T.M. Roll Shop Water		
Total Chromium	0.1	0.2
Total Hexavalent Chrome	0.1	BDL
EP TOX METALS		
Sample #84" H.S.M. Roll Shop Sludge		
EP TOX Hexavalent Chrome	0.1	1.4
EP TOX Chromium	0.1	1.5
Sample #84" H.S.M. Roll Shop Water		
EP TOX Hexavalent Chrome	0.1	BDL
EP TOX Chromium	0.1	BDL
Sample #3 S.M. Roll Shop Sludge		
EP TOX Hexavalent Chrome	0.1	BDL
EP TOX Chromium	0.1	0.3
Sample #3 S.M. Roll Shop Water		
EP TOX Hexavalent Chrome	0.1	BDL
EP TOX Chromium	0.1	0.2
Sample #2 T.M. Roll Shop Sludge		
EP TOX Hexavalent Chrome	0.1	2.3
EP TOX Chromium	0.1	4.2

QUALITY
ANALYTICAL
LABS, INC.

Parameter	MDL (ppm)	Analysis (ppm)
Sample #2 T.M. Roll Shop Water		
EP TOX Hexavalent Chrome	0.1	BDL
EP TOX Chromium	0.1	0.2

MDL = Method Detection Limit
BDL = Below Detection Limit

Respectfully submitted,

Nicholas Cuzzone
Lab Manager
Quality Analytical Labs, Inc.

QUALITY
ANALYTICAL
LABS, INC.

April 19, 1991

LTV Steel
3001 Dickey Road
East Chicago, IN 46312

Attn: Mohammed Babar

Dear Mr. Babar:

This letter will serve as the QA/QC report for analytical work done on COC #7650.

Hexavalent Chromium:	Sample conc.	spike am't	Rec.
Sample #1 H.S.M. Roll Shop Sludge	9.6 ppm	2.5 ppm	86%
Sample #3 S.M. Roll Shop Sludge E.P. Tox	<0.1 ppm	1.0 ppm	90%

Total Chrome:	Sample conc.	spike am't	Rec.
Sample #1 84" Roll Shop Sludge	1430 ppm	25 ppm	88%
Sample #2 T.M. Roll Shop Sludge E.P. Tox	4.2 ppm	1.0 ppm	90%

The method blanks were all Below Detection Limits of the method used.

Should you need any further information, please feel free to contact me.

Sincerely,

Nick Cuzzone
Lab Manager
Quality Analytical Labs, Inc.

NATIONAL ENVIRONMENTAL TESTING, INC.

NET Midwest, Inc.
Indianapolis Division
6964 Hillsdale Court
Indianapolis, IN 46250
Tel: (317) 842-4261
Fax: (317) 842-4286

ANALYTICAL REPORT

Mr. Mohammad Babar
LTV STEEL
3001 Dicky Road
East Chicago, IN 46312

04-09-91

P.O. NO.: 308146

Page 1

Date Received: 03-26-91

Sample Number/ Parameters	Sample I.D. Results	Sample Date/ Units
36412	84 HOT STRIP MILL ROLL SHOP SLUDGE	03-25-91
Chromium, Hexavalent	<1.0 .001 mg/L	ug/g
Chromium, Total	3900. 3.9 mg/L	ug/g
EP Tox - Chromium	<0.04	mg/L
EP Tox - Chromium, Hex.	<1.0	mg/L
36413	#2 TIN MILL ROLL SHOP SLUDGE	03-25-91
Chromium, Hexavalent	<10. <.01 mg/L	ug/g
Chromium, Total	1600. 1.6 mg/L	ug/g
EP Tox - Chromium	0.61	mg/L
EP Tox - Chromium, Hex.	<10.	mg/L
36414	#3 SHEET MILL ROLL SHOP SLUDGE	03-25-91
Chromium, Hexavalent	<10. <.01 mg/L	ug/g
Chromium, Total	3300. 3.3 mg/L	ug/g
EP Tox - Chromium	1.5	mg/L
EP Tox - Chromium, Hex.	<10.	mg/L

Karen Groleau

Karen Groleau
Project Manager

NATIONAL ENVIRONMENTAL TESTING, INC.

NET Midwest, Inc.
Indianapolis Division
6964 Hillsdale Court
Indianapolis, IN 46250
Tel: (317) 842-4261
Fax: (317) 842-4286

ANALYTICAL REPORT

Mr. Mohammad Babar
LTV STEEL
3001 Dicky Road
East Chicago, IN 46312

04-09-91

P.O. NO.: 308146

Date Received: 03-26-91

Sample Number/ Parameters	Sample I.D.	Results	Sample Date/ Units
36409	#3 SHEET MILL ROLL SHOP WATER		03-25-91
EP Tox - Chromium		0.95	mg/L
EP Tox - Chromium, Hex.		<1.0	mg/L
36410	#2 TIN MILL ROLL SHOP WATER		03-25-91
EP Tox - Chromium		0.15	mg/L
EP Tox - Chromium, Hex.		<1.0	mg/L
36411	84 HOT STRIP MILL ROLL SHOP WATER		03-25-91
EP Tox - Chromium		<0.04	mg/L
EP Tox - Chromium, Hex.		<1.0	mg/L

Karen Groleau

Karen Groleau
Project Manager

NET NATIONAL ENVIRONMENTAL TESTING, INC.

NET Midwest, Inc.
Indianapolis Division
6964 Hillsdale Court
Indianapolis, IN 46250
Tel: (317) 842-4261
Fax: (317) 842-4286

INORGANIC QA/QC DATA

Client Name: LTV STEEL

Project ID :

NET Lab No.: 36409 - 36414

Parameter	Date Analyzed	Prep Blk mg/l	ICV Found	ICV True	ICV %Rec.	Accuracy MS	Accuracy %Rec.	Precision MSD	Precision RPD
36409 Hex. Cr-EPTox	3-29-91	<0.01	0.142	0.15	94	0.229	91	0.233	1.7
36410 Hex. Cr-EPTox	3-28-91	<0.01	0.147	0.15	98	0.232	93	0.234	0.8
36411 Hex. Cr-EPTox	3-28-91	<0.01	0.147	0.15	98	0.135	89	0.135	0
36412 Hex. Cr	3-28-91	<0.01	0.147	0.15	98	0.232	93	0.231	0.4
36412 Hex. Cr-EPTox	3-29-91	<0.01	0.142	0.15	94	0.229	91	0.229	0
36413 Hex. Cr	3-28-91	<0.01	0.147	0.15	98	0.232	93	0.236	1.7
36413 Hex. Cr-EPTox	3-29-91	<0.01	0.142	0.15	94	0.236	94	0.239	1.1
36414 Hex. Cr	3-28-91	<0.01	0.147	0.15	98	0.237	95	0.237	0
36414 Hex. Cr-EPTox	3-29-91	<0.01	0.142	0.15	94	0.218	87	0.216	0.6
Tot. Cr	4-9-91	<0.04	0.383	0.444	*86	0.453	91	0.454	0.2
Tot. Cr-EPTox	4-9-91	<0.04	0.383	0.444	*86	0.453	91	0.454	0.2

Advisory Control Limits:

Prep Blank - should be less than the reporting limit.
Independent Calibration Verification (ICV) - should get 90-110% Recovery.
Accuracy - should get 75-125% Recovery for Matrix Spike.
Precision - should get <20% Relative Percent Difference for MS/MSD.

Comments: * VENDORS CONTROL LIMITS: 0.344-0.538 OR 77-121 % RECOVERY

QA/QC Data Reviewed By: Bert Day Date: 4-9-91

NET NATIONAL ENVIRONMENTAL TESTING, INC.

NET Midwest, Inc.
Indianapolis Division
6964 Hillsdale Court
Indianapolis, IN 46250
Tel: (317) 842-4261
Fax: (317) 842-4266

INORGANIC QA/QC DATA

Client Name: LTV STEEL

Project ID :

NET Lab No.: 36409 - 36414

Parameter	Date Analyzed	Prep Blk mg/l	ICV Found	ICV True	ICV %Rec.	Accuracy MS	Accuracy %Rec.	Precision MSD	Precision RPD
36409 Hex. Cr-EPTox	3-29-91	<0.01	0.142	0.15	94	0.229	91	0.233	1.7
36410 Hex. Cr-EPTox	3-28-91	<0.01	0.147	0.15	98	0.232	93	0.234	0.8
36411 Hex. Cr-EPTox	3-28-91	<0.01	0.147	0.15	98	0.135	89	0.135	0
36412 Hex. Cr	3-28-91	<0.01	0.147	0.15	98	0.232	93	0.231	0.4
36412 Hex. Cr-EPTox	3-29-91	<0.01	0.142	0.15	94	0.229	91	0.229	0
36413 Hex. Cr	3-28-91	<0.01	0.147	0.15	98	0.232	93	0.236	1.7
36413 Hex. Cr-EPTox	3-29-91	<0.01	0.142	0.15	94	0.236	94	0.239	1.1
36414 Hex. Cr	3-28-91	<0.01	0.147	0.15	98	0.237	95	0.237	0
36414 Hex. Cr-EPTox	3-29-91	<0.01	0.142	0.15	94	0.218	87	0.216	0.6
Tot. Cr	4-9-91	<0.04	0.383	0.444	*86	0.453	91	0.454	0.2
Tot. Cr-EPTox	4-9-91	<0.04	0.383	0.444	*86	0.453	91	0.454	0.2

Advisory Control Limits:

Prep Blank - should be less than the reporting limit.
Independent Calibration Verification (ICV) - should get 90-110% Recovery.
Accuracy - should get 75-125% Recovery for Matrix Spike.
Precision - should get <20% Relative Percent Difference for MS/MSD.

Comments: * VENDORS CONTROL LIMITS: 0.344-0.538 OR 77-121 % RECOVERY

QA/QC Data Reviewed By: Bert Day Date: 4-9-91

REFERENCE 7

ATEC Associates, Inc.
2646 Highway Avenue
Highland, Indiana 46322
[219] 972-5252, [312] 375-9092
FAX # [312] 375-8649

February 26, 1991
File 52-08040

Mr. Rick Meyers
LTV Steel
3001 Dickey Road
East Chicago, IN 46312-1610

Re: Six Samples for EPTOX Chromium, Hexavalent Chromium ande Total Chromium

Dear Mr. Meyers:

Enclosed are the results of the Chemical Analyses for the six samples which were submitted to the ATEC Environmental/Analytical Testing Division on February 11, 1991, on behalf of LTV Steel. Metals were analyzed on a Leeman Lab PS1000 ICP according to SW 846 Method 6010.

All associated quality control information will be maintained in the Testing Division files, a copy of which can be forwarded to you upon request. After a thirty-day period, a fee will be assessed for this additional information.

It has been a pleasure serving you and, as always, if there are any questions concerning these results or the ATEC Policies, please feel free to contact me.

Respectfully submitted,
ATEC Associates, Inc.

Aaron Simpson
Environmental/Analytical
Testing Division

REPORT OF TEST RESULTS

Client: LTV Steel

Sample Matrix: Sludge
Sample Taken By: Client
Date Sampled: February 11, 1991
Date Received: February 11, 1991
ATEC Lab Number: 910082
ATEC Project Number: 52-08040

PARAMTER (unit in mg/L unless noted)	SAMPLE I.D. NUMBER 3 S.M. SLUDGE	2 T.M. SLUDGE	84"H.S.M. SLUDGE	QUANTI-TATION LIMIT	SW 846 METHOD NO.
EPTOX Chromium	7.5	<0.5	2.2	0.5	6010
Total Chromium (mg/kg)	7600	5800	14000	5.0 mg/kg	6010

Respectfully submitted,
ATEC Associates, Inc.

Elizabeth Brown
Environmental/Analytical
Testing Division

REPORT OF TEST RESULTS

Client: LTV Steel

Sample Matrix: Water
Sample Taken By: Client
Date Sampled: February 11, 1991
Date Received: February 11, 1991
ATEC Lab Number: 910082
ATEC Project Number: 52-08040

PARAMTER (unit in mg/L unless noted)	SAMPLE I.D. NUMBER 3 S.M. H2O	2 T.M. H2O	84"H.S.M. H2O	QUANTI-TATION LIMIT	SW 846 METHOD NO.
Total Chromium	1.6	22	1.6	0.5	6010

Respectfully submitted,
ATEC Associates, Inc.

Elizabeth Brown
Environmental/Analytical
Testing Division

CASE NARRATIVE

All samples were analyzed for hexavalent chromium [Cr(VI)] within 24 hours of receipt or extraction.

Hexavalent chromium as received was requested for three sludge samples. Unable to do a direct determination, we submitted the sludges for a neutral leachate extraction. The results submitted reflect the dissolved hexavalent chromium present in the neutral leachate extract.

As requested, three EPTOX extracts were tested for hexavalent chromium. A duplicate and two spikes were performed on each of the extracts. As shown in the inorganic quality control summary, all spike recoveries for these extracts fell far below the acceptable limits for this test. With these low recoveries possibly indicating a suppressive interference, the extracts were then diluted and reanalyzed. Again, spike recoveries fell far below the acceptable limits. Further effort was made to adjust the pH of the acidic extract to rule out the presence of a residual reducing agent. This also proved unsuccessful.

INORGANIC
QUALITY CONTROL SUMMARY

MATRIX: WATER SOIL SLUDGE OTHER_____

PERCENT SOLIDS:_____ DRY WEIGHT [ ] AS RECEIVED [ ]

TEST	EXTRACTION DIGESTION/ PREP DATE	ANALYSIS DATE	QUANT. LIMIT	METHOD BLANK	METHOD STANDARD	T.V.	% REC.	SAMPLE I.D.	SAMPLE RESULT	DUPLICATE RESULT	% RSD	SPIKE RESULT	SPIKE T.V.	% REC.
NEUTRAL LEACHATE ON SLUDGE														
Cr+6	2-12-91	2-13-91	0.02	<0.02	0.495	0.5	99	082-1N	0.027	0.027	0	0.456	0.5	86
Cr+6	2-12-91	2-13-91	0.02					082-2N	<0.02	<0.02	NA	0.495	0.5	99
Cr+6	2-12-91	2-13-91	0.02					082-3N	<0.02	<0.02	NA	0.495	0.5	99
WATER ANALYSIS														
Cr+6		2-11-91	0.02	<0.02	0.495	0.5	99	082-4	0.90			1.07	0.17	100
Cr+6		2-11-91	0.02					082-5	0.06			0.15	0.1	90
Cr+6		2-11-91	0.02					082-6	<0.02	<0.02	NA	0.495	0.5	99
SLUDGE EPTOX														
Cr+6	2-12-91	2-13-91	0.02	<0.02	0.495	0.5	99	082-1	0.02	0.02	0	0.03	0.5	2
Cr+6	2-12-91	2-13-91	0.02					082-1				0.02	1.0	0
Cr+6	2-12-91	2-13-91	0.02					082-2	<0.02	<0.02	NA	0.02	0.5	4
Cr+6	2-12-91	2-13-91	0.02					082-2				0.03	1.0	3
Cr+6	2-12-91	2-13-91	0.02					082-3	<0.02	<0.02	NA	<0.02	0.5	0
Cr+6	2-12-91	2-13-91	0.02					082-3				<0.02	1.0	0

REPORT OF TEST RESULTS

Client: LTV Steel

Sample Matrix: Sludge
Sample Taken By: Client
Date Sampled: February 11, 1991
Date Received: February 11, 1991
ATEC Lab Number: 910082
ATEC Project Number: 52-08040

NEUTRAL LEACHATE PARAMTER (unit in mg/L unless noted)	SAMPLE I.D. NUMBER 3 S.M. SLUDGE	2 T.M. SLUDGE	84"H.S.M. SLUDGE	QUANTI-TATION LIMIT	SW 846 METHOD NO.
Hexavalent Chromium	0.03	<0.02	<0.02	0.02	7196

Respectfully submitted,
ATEC Associates, Inc.

Elizabeth Brown
Environmental/Analytical
Testing Division

REPORT OF TEST RESULTS

Client: LTV Steel

Sample Matrix: Water
Sample Taken By: Client
Date Sampled: February 11, 1991
Date Received: February 11, 1991
ATEC Lab Number: 910082
ATEC Project Number: 52-08040

PARAMTER (unit in mg/L unless noted)	SAMPLE I.D. NUMBER 3 S.M. H2O	2 T.M. H2O	84"H.S.M. H2O	QUANTI-TATION LIMIT	SW 846 METHOD NO.
Hexavalent Chromium	0.9	0.06	<0.02	0.02	7196

Respectfully submitted,
ATEC Associates, Inc.

Elizabeth Brown
Environmental/Analytical
Testing Division

REPORT OF TEST RESULTS

Client: LTV Steel

Sample Matrix: Sludge
Sample Taken By: Client
Date Sampled: February 11, 1991
Date Received: February 11, 1991
ATEC Lab Number: 910082
ATEC Project Number: 52-08040

PARAMTER (unit in mg/L unless noted)	SAMPLE I.D. NUMBER 3 S.M. SLUDGE	2 T.M. SLUDGE	84"H.S.M. SLUDGE	QUANTI-TATION LIMIT	SW 846 METHOD NO.
EPTOX					
Hexavalent Chromium	* 0.02	* <0.02	* <0.02	0.02	7196

* Matrix Interference Suspected. See Case Narrative.

Respectfully submitted,
ATEC Associates, Inc.

Elizabeth Brown
Environmental/Analytical
Testing Division

910082

ATEC Associates, Inc.
LAB WORK ORDER
CHEMISTRY LAB

JOB NUMBER 52-08040 DATE ASSIGNED 2-11-91

JOB NAME LTV Steel DATE REQUIRED 2-25-91

LOCATION

CLIENT (BILLING INFO)

SAMPLE (CIRCLE) - POSSIBLE HAZARDOUS MATERIALS (SPECIAL HANDLING MAY BE REQUIRED) ☐ YES ☐ NO

SOIL COAL ASBESTOS (BULK OR AIR SAMPLE)

ROOFING WATER (WASTE OR WELL) SOLID WASTE

OTHER Sludge

SAMPLE I.D.	TEST REQUIRED (eg pH, metals, TOX, BOD, Asbestos)	COMPUTER BILLING CODE
3S.M.Sludge	{Cr+6, EP TOX Cr} {Total Cr, Cr+6 As Rec.}	910082-1
2T.M.Sludge		-2
84" H.S.M.Sludge		-3
3S.M.H2O		-4
2T.M.H2O		-5
84" H.S.M.H2O		-6

SAMPLE LOCATION: ☐ LIBRARY ☐ CHEM LAB ☐ MAIN LAB

SPECIAL INSTRUCTIONS:

☐ OKAY TO INVOICE

ASSIGNED BY:

WHITE - ORIGINAL (WORKING COPY) YELLOW - FILE COPY PINK - ENGINEERING COPY

CHAIN OF CUSTODY RECORD

PROJ. NO. 52-08040

PROJECT NAME ROLL SHOP CHROME

CLIENT LTV STEEL

LAB PROJ. NO.

SAMPLERS: (Signature) Mohammad Babar

SAMPLING METHOD

LABORATORY ANALYSIS

SAMPLE I.D. NO.	DATE	TIME	COMPOSITE	GRAB	WATER	SOIL	SLUDGE	FILTERED	ACIDIFIED	ICED		NUMBER OF CONTAINERS	LAB I.D. NUMBER	VOLATILE ORGANICS	BTX & E	TOTAL HYDROCARBONS	PCB'S	E.P. TOXIC METALS	TOTAL METALS (8)	IGNITABILITY	EPTOX Cr	Cr+6	TOTAL Cr As Pb Cd	SAMPLE LOCATION / REMARKS Cr+6 As Pb Cd
3S.M SLUDGE	2-11-91						X					1								X	X	X		X
2T.M SLUDGE	"						X					1								X	X	X		X
84" H.S.M SLUDGE	"						X					1								X	X	X		X
3S.M H_2O	"				X							1								X	X			
2T.M H_2O	"				X							1								X	X			
84" H.S.M H_2O	"				X							1								X	X			

9100821-1
-2
-3
-4
-5
-6

ATEC Environmental Consultants
Division of ATEC Associates, Inc.
1501 East Main Street
Griffith, Indiana 46319-0270
(219) 924-6690, FAX # (312) 375-8649

Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Mohammad Babar	2/11/91 10:00 AM				

Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Project Manager / Phone #:
		Elizabeth Brown	2/11/91 10:00 AM.	

CHEMISTRY DIVISION

STATEMENT OF CHARGES

Date: February 26, 1991

Client: LTV Steel
3001 Dickey Road
East Chicago, IN 46312-1610

Client Project Number: 52-08040
Laboratory Invoice No.: 910082
Client Project Manager: Rick Meyers

SERVICES PERFORMED

Item No.	Quantity	Description	Unit Price	Total Price
1	3	EPTOX Cr	136.00	408.00
2	6	Total Cr	40.00	240.00
3	6	Hexavalent Cr	35.00	315.00
			Invoice Total	$963.00

* Please do not pay. This is only a statement of charges. An invoice will be forth coming.

METHOD 7196

CHROMIUM, HEXAVALENT (COLORIMETRIC)

1.0 SCOPE AND APPLICATION

1.1 Method 7196 is used to determine the concentration of dissolved hexavalent chromium [Cr(VI)] in Extraction Procedure (EP) toxicity characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present (see Paragraph 3.1 below).

1.2 Method 7196 may be used to analyze samples containing from 0.5 to 50 mg of Cr(VI) per liter.

2.0 SUMMARY OF METHOD

2.1 Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, may be determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet color of unknown composition is produced. The reaction is very sensitive, the absorbancy index per gram atom of chromium being about 40,000 at 540 nm. Addition of an excess of diphenylcarbazide yields the red-violet product, and its absorbance is measured photometrically at 540 nm.

3.0 INTERFERENCES

3.1 The chromium reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere if the chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react to form color with the reagent; however, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/L of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble.

3.2 Iron in concentrations greater than 1 mg/L may produce a yellow color, but the ferric iron color is not strong and difficulty is not normally encountered if the absorbance is measured photometrically at the appropriate wavelength.

4.0 APPARATUS AND MATERIALS

4.1 Colorimetric equipment: One of the following is required: Either a spectrophotometer, for use at 540 nm, providing a light path of 1 cm or longer, or a filter photometer, providing a light path of 1 cm or longer and equipped with a greenish-yellow filter having maximum transmittance near 540 nm.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Potassium dichromate stock solution: Dissolve 141.4 mg of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in Type II water and dilute to 1 liter (1 mL = 50 ug Cr).

5.3 Potassium dichromate standard solution: Dilute 10.00 mL potassium dichromate stock solution to 100 mL (1 mL = 5 ug Cr).

5.4 Sulfuric acid, 10% (v/v): Dilute 10 mL of distilled reagent grade or spectrograde quality sulfuric acid, H_2SO_4, to 100 mL with Type II water.

5.5 Diphenylcarbazide solution: Dissolve 250 mg 1,5-diphenylcarbazide in 50 mL acetone. Store in a brown bottle. Discard when the solution becomes discolored.

5.6 Acetone (analytical reagent grade): Avoid or redistill material that comes in containers with metal or metal-lined caps.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Since the stability of Cr(VI) in EP extracts is not completely understood at this time, the analysis should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, the samples and extracts should be stored at 4°C until analyzed. The maximum holding time prior to analysis is 24 hr.

7.0 PROCEDURE

7.1 Color development and measurement: Transfer 95 mL of the extract to be tested to a 100-mL volumetric flask. Add 2.0 mL diphenylcarbazide solution and mix. Add H_2SO_4 solution to give a pH of 2 ± 0.5, dilute to 100 mL with Type II water, and let stand 5 to 10 min for full color development. Transfer an appropriate portion of the solution to a 1-cm absorption cell and measure its absorbance at 540 nm. Use Type II water as a reference. Correct the absorbance reading of the sample by subtracting the absorbance of a blank carried through the method (see Note below). An aliquot of the sample containing all reagents except diphenyl semicarbazide should be prepared and used to correct the sample for turbidity (i.e., a turbidity blank). From the

corrected absorbance, determine the mg/L of chromium present by reference to the calibration curve.

NOTE: If the solution is turbid after dilution to 100 mL in Step 7.1, above, take an absorbance reading before adding the carbazide reagent and correct the absorbance reading of the final colored solution by subtracting the absorbance measured previously.

7.2 Preparation of calibration curve:

7.2.1 To compensate for possible slight losses of chromium during digestion or other operations of the analysis, treat the chromium standards by the same procedure as the sample. Accordingly, pipet a chromium standard solution in measured volumes into 250-mL beakers or conical flasks to generate standard concentrations ranging from 0.5 to 5 mg/L Cr(VI) when diluted to the appropriate volume.

7.2.2 Develop the color of the standards as for the samples. Transfer a suitable portion of each colored solution to a 1-cm absorption cell and measure the absorbance at 540 nm. As reference, use Type II water. Correct the absorbance readings of the standards by subtracting the absorbance of a reagent blank carried through the method. Construct a calibration curve by plotting corrected absorbance values against mg/L of Cr(VI).

7.3 Verification:

7.3.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting color development. This must be accomplished by analyzing a second 10-mL aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstances should the increase be less than 30 g Cr(VI)/liter. To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.3.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

7.3.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

7.3.4 If the interference persists after sample dilution, an alternative method (Method 7195, Coprecipitation, or Method 7197, Chelation/Extraction) should be used.

7.4 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is

obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified..

7.5 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions (see Method 7000, Section 8.7).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.3 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.4 Verify calibration with an independently prepared check standard every 15 samples.

8.5 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

8.6 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

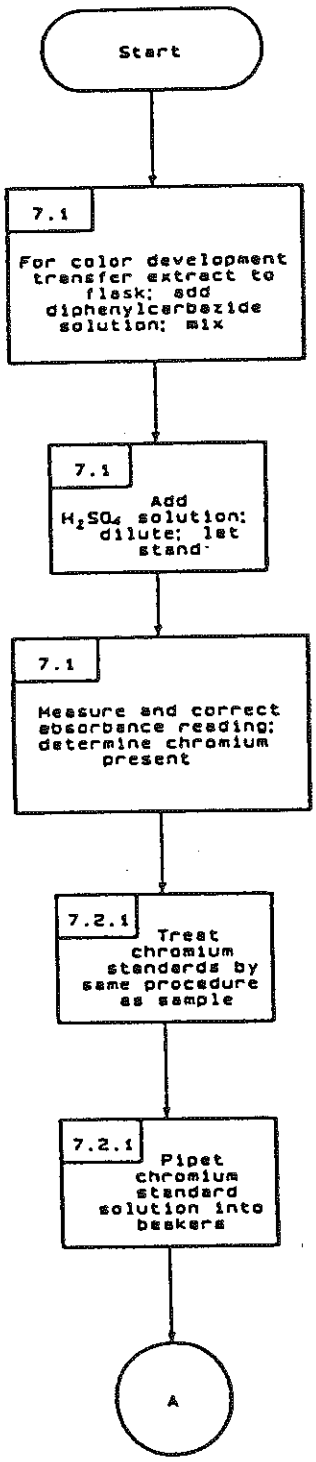
10.0 REFERENCES

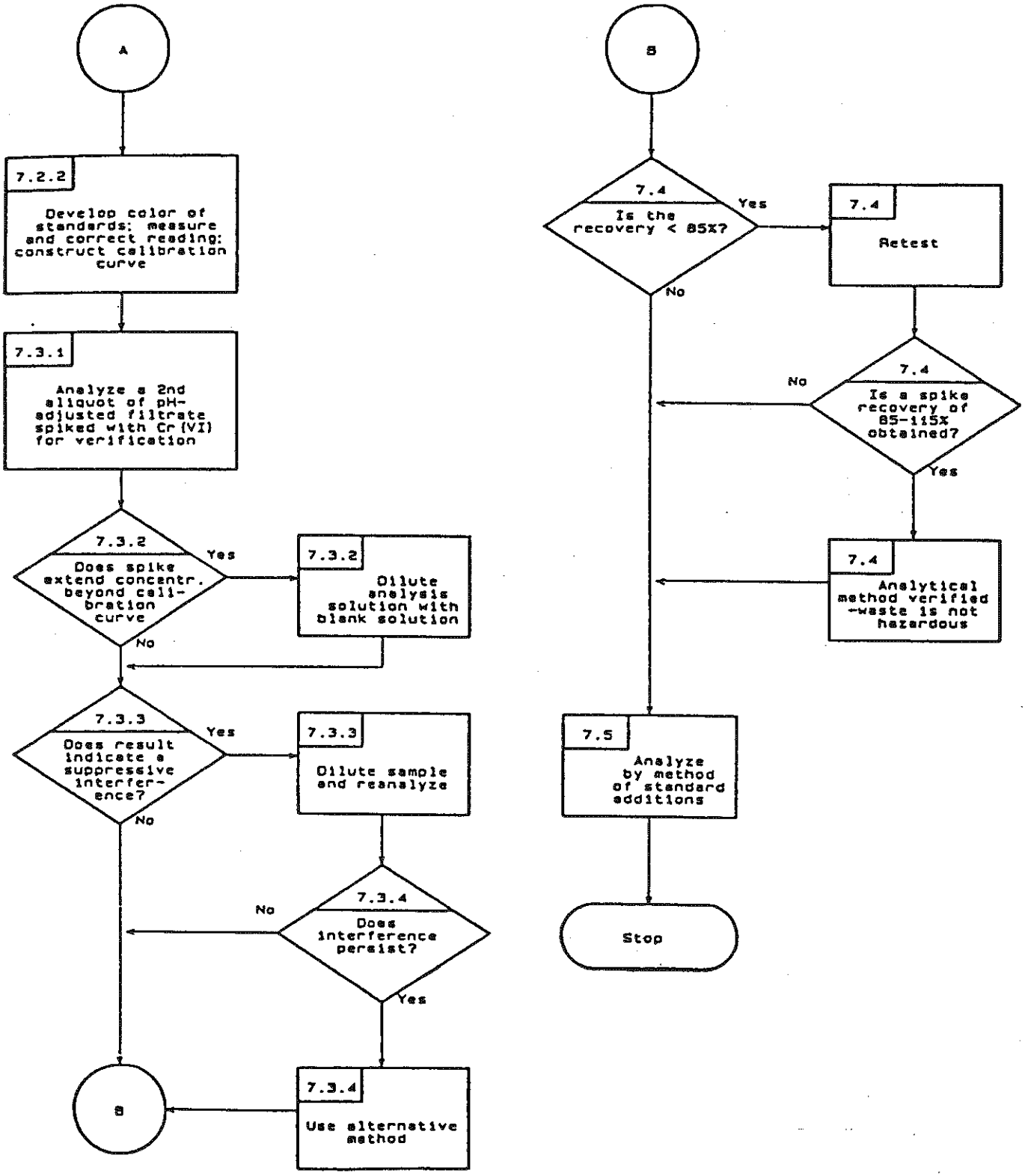
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Methods 218.4 and 218.5.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	Not known	0.096, 0.107 ug/g
Sediment from chemical storage area	3060	115, 117 ug/g


Start
7.1
For color development transfer extract to flask; add diphenylcarbazide solution; mix
7.1
Add H_2SO_4 solution; dilute; let stand
7.1
Measure and correct absorbance reading; determine chromium present
7.2.1
Treat chromium standards by same procedure as sample
7.2.1
Pipet chromium standard solution into beakers
A


A
7.2.2
Develop color of standards; measure and correct reading; construct calibration curve
7.3.1
Analyze a 2nd aliquot of pH-adjusted filtrate spiked with Cr(VI) for verification
7.3.2
Does spike extend concentr. beyond calibration curve
Yes
No
7.3.2
Dilute analysis solution with blank solution
7.3.3
Does result indicate a suppressive interference?
Yes
No
7.3.3
Dilute sample and reanalyze
7.3.4
Does interference persist?
No
Yes
7.3.4
Use alternative method
B
B
7.4
Is the recovery < 85%?
Yes
No
7.4
Retest
7.4
Is a spike recovery of 85-115% obtained?
No
Yes
7.4
Analytical method verified -waste is not hazardous
7.5
Analyze by method of standard additions
Stop

RECEIVED
FEB 15 1991
ENVIRONMENTAL CONTROL

See pg 3

MINUTES OF MEETING

DATE OF MEETING: February 5, 1991

TIME: 1:00 p.m.

LOCATION: Indianapolis, IDEM, 9th Floor Conference Room

SUBJECT: LTV Steel - Indiana Harbor Works, Proposed On-Site Landfill

ATTENDEES:

George Oliver, IDEM
Daniela Klesmith, IDEM
Pam O'Rourke, IDEM
Bruce Kizer, IDEM
Rob Dunlan, IDEM
Greg Lorenz, IDEM
Devassy Koottungal, IDEM
Christa Russell, IDEM
David Becka, IDEM
Carl Broman, LTV Steel
Rick Myers, LTV Steel
Sam DiCera, LTV Steel
Max Kitchel, Baker/TSA

A. **INTRODUCTION**

G. Oliver, IDEM, opened the meeting with a brief introduction of IDEM personnel attending the meeting and that he understood there were two subjects for discussion:

1. IHW waste classifications based on waste characterization study submitted April 1990.

2. Preliminary discussions of LTV Steel IHW conceptual on-site special/restricted waste landfill.

C. Broman followed with introductions of LTV Steel and Baker/TSA representatives and indicated that two key personnel, LTV Steel corporate representative, L. Szuhay, and Baker/TSA project manager, J. Quay, were unable to attend due to flight cancellations resulting from fog at the Indianapolis airport.

B. **IHW WASTE CLASSIFICATIONS**

G. Lorenz, IDEM Special Projects, indicated he had conversed with R. Myers about the two wastestreams (i.e., BOF precipitator dust and roll shop swarf) that are being reviewed based on the exclusions identified in the waste characterization study.

B. Kizer, IDEM Hazardous Waste Compliance, then indicated that based on his review of the Bevill Amendment exclusion, BOF precipitator dust currently is excluded as a hazardous waste. However, he added that this list of Bevill exclusions has the potential to be revised and that BOF precipitator dust could become a characteristically hazardous waste if this exclusion is deleted.

B. Kizer indicated he had concerns about the roll shop wastes exclusion based on the non-hexavalent chromium exclusion. After a lengthy discussion about the waste generating process, it was concluded that additional information would be required before an accurate evaluation of the exclusion could be developed.

DATE OF MEETING: February 5, 1991

Item No.	Description
	Additional information requested is listed below:
✓	1. Additional clarification on the waste generating process (i.e., roll grinding).
✓	2. Analyses of wastes from all three roll shops separately, not a composite of the three waste streams. That is, individual analysis of roll shop swarf from No. 2 Tin Mill, No. 3 Cold Strip and the Hot Strip Mill.
✓	3. Analysis of the liquid/water effluent from each process to determine the presence of hexavalent chrome.
waste up *	4. Provide information on the chrome plating process to determine hexavalent/trivalent chrome presence. Note: IDEM was informed that all roll chrome plating processes are performed off-site by outside contractors.
*	5. Provide information that during waste mixing or co-mingling, a non-oxidizing environment is present to prevent trivalent to hexavalent conversion.
C.	CONCEPTUAL ON-SITE LANDFILL
	Max Kitchel initiated discussion by indicating there were three primary objectives for the LTV Steel/IDEM meeting:
	1. Inform IDEM of LTV Steel's potential pursuit of an on-site restricted waste landfill.
	2. Acquire IDEM's response to potential issuance of an on-site landfill permit to LTV Steel.
	3. Acquire IDEM's response to the concept that LTV Steel would design for Type I parameters but permit and operate at Type III standards.
	In regards to items 1 and 2, C. Russel indicated that IDEM was working with other industry in that part of the state in order to develop a viable plan to better manage waste handling and disposal along the lake.
	A matrix-type table was distributed that presented leachate concentrations of ATEC's stabilized/treated wastes compared to 329 IAC 2 Type III and Type IV concentrations. It was noted that with the exception of TDS (total dissolved solids) and pH, all leachate concentrations were within the Type III and Type IV ranges.
	M. Kitchel indicated that LTV Steel might request a Type III classification with variances based on the TDS and pH parameters to help LTV Steel reduce overall

DATE OF MEETING: February 5, 1991

Item No.	Description
	project cost and maximize the landfill lifetime through reduction of the cover requirements.
	Following extended discussion on the various requirements of Type III versus Type I. G. Oliver indicated IDEM would be more comfortable with potentially issuing a Type I with exclusions rather than a Type III with variances.
when ?	The meeting closed with IDEM indicating that LTV Steel should submit a general plan with the intended engineering design, location and anticipated operation. IDEM would review this and respond accordingly.

cc: K. Grant - LTV Steel
S. Houk - LTV Steel
G. McDaniel - LTV Steel
A. McRainey - LTV Steel
H. L. Page - LTV Steel
D. E. Papajcik - LTV Steel
N. Pillarella - LTV Steel
L. Szuhay - LTV Steel

REFERENCE 9

RECEIVED
MAY 31 1991
ENVIRONMENTAL CONTROL

LTV Steel Company

May 29, 1991

Richard L. Myers
Environmental Engineer
LTV Steel Company
3001 Dickey Road
East Chicago, Indiana 46312-1610
(219) 391-2864

George Oliver, Chief
Special Projects Section
Solid Waste Management Branch
Indiana Department of Environmental Management
105 South Meridian Street
P.O. Box 6015
Indianapolis, IN 46206-6015

Re: Study of Roll Shop Waste

Dear Mr. Oliver:

The enclosed study is a follow-up to the February 5, 1991 meeting with you and other IDEM personnel. In that meeting a clarification of the process generating Roll Shop Waste was requested. LTV Steel was also asked to go into more detail as to how Indiana Rule 329 IAC 3-3-4(b)(6)(A) applies to Roll Shop Waste.

If you have any questions regarding the enclosed informaiton, please do not hesitate to call me at (219) 391-2864.

Very truly yours,

LTV STEEL COMPANY

Richard L. Myers
Environmental Engineer
Indiana Harbor Works

RLM:mz
cc: file

bcc: M.Z. Babar - w/encl.
C. Broman - w/o encl.
S. Di Cera - w/o encl.
L.A. Szuhay - w/encl.

STUDY OF ROLL SHOP WASTE

LTV STEEL COMPANY
3001 DICKEY ROAD
EAST CHICAGO, INDIANA

May 1991

TABLE OF CONTENTS

I INTRODUCTION

II PROCESS DESCRIPTIONS

III THE EXCLUSION RULE

IV APPLICATION OF THE EXCLUSION RULE TO LTV's ROLL SHOP WASTES

V SUMMARY

VI TABLES

VII REFERENCES

VIII LABORATORY DATA

I. Introduction

In August of 1990, LTV Steel Company, Inc. (LTV) submitted information regarding on-site solid waste activities to IDEM. Upon review of that information, IDEM requested that LTV submit additional waste characterization data in accordance with Indiana Solid Waste Rules 329 IAC 2-9. Roll shop waste, one of the waste streams included in the waste characterization study, exhibited chromium concentrations exceeding the threshold limit for Type I restricted waste classification in two of the three samples. LTV Steel believes that the roll shop waste is excluded from hazardous waste regulations based upon the exclusion listed in Indiana Rule 329 IAC 3-3-4(b)(6)(A), which exempts non-hexavalent chromium wastes.

During a meeting at IDEM offices in Indianapolis on February 5, 1991, IDEM requested LTV submit additional data on roll shop waste. LTV was asked to individually characterize the roll shop waste from each of the three roll shops, as opposed to compositing the wastes as was done in the first submittal. A more complete process description of the roll shops was also requested. LTV was asked to go into more detail as to how the cited exclusion applied to LTV's roll shop wastes. Sampling and analysis of the water from the roll shop grinders were also requested.

LTV conducted waste sampling of the roll shop wastes and coolants as outlined in the previous waste characterization study. The sampling was performed over a seven (7) week period from February 11 to March 25. The laboratory analytical work was performed by three different, independent laboratories. Although all three laboratories encountered difficulties in performing those analyses, LTV Steel believes that this data will allow IDEM to grant the non-hexavalent chromium exclusion of Indiana Rule 329 IAC 3-3-4(b)(6)(A).

II. Process Descriptions

General Overview

In a flat rolled steel producing operation, various rolling operations are utilized to produce a variety of steel coils. Over time these rolls, due to extreme mechanical and thermal stresses, develop various surface defects which reduce the quality of the finished product. Damaged rolls, however, can be resurfaced to restore a smooth, level surface by grinding them in a roll shop. All of the alloy steel rolls used at LTV are ground in one of three roll shops, strategically located in each mill.

Each of the three roll shop stations serves the same general function - to remove imperfections on steel roll surfaces. Each station utilizes a process whereby a damaged steel roll is placed in a grinding lathe and ground while a coolant, consisting mostly of water, is sprayed at the point of contact to remove friction heat created by the grinding process. To provide a better understanding of the operation of LTV's roll shops, each is described in greater detail in the ensuing sections.

A. 84" Hot Strip Mill (HSM) Roll Shop

The 84" HSM Roll Shop services all of the rolls utilized at the Hot Strip Mill. The rolls are used in the operation where steel slabs are reduced to coils.

A. 84" Hot Strip Mill (HSM) Roll Shop (cont'd)

The rolls develop surface defects as the slabs are reduced. Rolls with surface defects are taken to the roll shop where they are ground to a uniform surface. The roll is sprayed with water at the point of contact with the grinding wheel to remove the heat of friction generated during the grinding process. There are a total of 250 rolls at the Hot Strip Mill, 178 of the rolls have a metallic chrome content of about 1.5% while the other 72 contain 16% metallic chrome. Table 1 lists a typical analysis for each type of roll.

The slurry from the grinder, containing water plus roll shavings or swarf, is sent to a collection pit where it is gravity filtered in collection boxes to remove the shavings. The resulting sludge is collected in three 10 cubic yard hoppers while the water is channeled to the 84" Hot Strip Mill waste water treatment plant. The sludge (approximately 10 cubic yards per week) is disposed of at our on-site landfill.

B. No. 3 Sheet Mill Roll Shop

The No. 3 Sheet Mill Roll Shop services and grinds all of the rolls at the #3 Sheet Mill plus rolls from the Hot Strip Finishing Mill. The #3 Sheet Mill generally processes coils produced at the 84" Hot Strip Mill and houses the pickle line, the 5-Stand Cold Reducing Mill and the Temper Mill. There are a total of 293

B. No. 3 Sheet Mill Roll Shop (cont'd)

serviced by this roll shop. All of the rolls are alloy steel or cast iron.

Table 2 lists a typical analysis of a steel roll serviced by the No. 3 Sheet Mill Roll Shop. The percentage of metallic chrome in the steel by weight is approximately 2.5%. Four rolls at the mill have a percentage of metallic chrome greater than 2.5%. These four rolls are utilized at the #3 Sheet Mill Temper Mill and contain 17% metallic chrome. Table 3 lists a typical analysis for one of those 4 rolls.

As the rolls are used in the mill they develop surface defects. A roll with surface defects is delivered to the roll shop to be ground to a smooth, level surface. To remove the friction heat generated during the grinding process, a coolant is sprayed onto the surface of the roll at the point of contact. This coolant consists of a 4% mixture of Quaker Chemical's QWERL RG, a complex carboxylic acid/amine mixture, and water.

The swarf and coolant slurry is collected and channeled to a skimming unit where separation of the liquid-solid mixture is accomplished. The separation unit is a closed system process whereby the waste stream enters the skimming unit from the underside and the solid particles are floated to the top. A mechanical rake mechanism continuously skims off the suspended

B. No. 3 Sheet Mill Roll Shop (cont'd)

particles into a 10 cubic yard box. The sludge (approximately 20 cubic yards per week) is hauled to the plant landfill for disposal. The effluent from the skimmer is passed through a portable screen filter to remove fine particles before being returned to the grinder to be reused as coolant. Makeup coolant is added to the system by an automatic control valve operating at a set point which regulates the amount of chemical being fed into a mixing chamber from a 10,000 gallon tank of Quaker QWERL RG.

C. #2 Tin Mill Roll Shop

The #2 Tin Mill complex houses a six-stand tandem mill, a temper mill, a tin plating line, a chrome plating line and a continuous annealing line. Three roll grinders are used to remove surface defects. Only the rolls from the temper mill and the tandem mill are serviced by the roll grinders. There are 300 rolls serviced by these roll grinders. Of the 300 rolls, approximately 150 are chrome plated following grinding. Chromium is plated on these rolls to a thickness of 0.003 inch by outside contractors. Table 4 contains a typical analysis for the alloy steel rolls.

As the rolls are ground, they are sprayed with a closed system coolant consisting of a mixture of Chemtool 650 (a monoethanolamine mixture), sodium carbonate and water. The slurry

C. #2 Tin Mill Roll Shop (cont'd)

(swarf and coolant) from the grinder is channeled to a collection pit where it is passed through a screen to filter out the solids. The filtered effluent is then pumped through another filter and returned to the grinder. Approximately once a month the sludge from the collection pits is removed, the water is decanted, and the solids (approximately 10 cubic yards/month) are deposited at the plant landfill. The decanted water enters the terminal lagoon and is treated by the on-site MSD Filtration Plant. After the pit is emptied, a fresh mixture of coolant is added to the system.

III. The Exclusion Rule

Wastes which fail the test for the characteristic of EP Toxicity because chromium is present in the waste may be excluded from hazardous waste regulation under Indiana Rule 329 IAC 3-3-4(b)(6)(A). The exclusion applies to wastes which are not listed hazardous wastes and to wastes which do not exhibit any other characteristics of hazardous waste. Further, the waste generator must demonstrate that the following three requirements are met:

1. The chromium in the waste is exclusively (or nearly exclusively) trivalent chromium; and

2. The waste is generated from an industrial process which uses trivalent chromium exclusively (or nearly exclusively) and the process does not generate hexavalent chromium; and

III. The Exclusion Rule (cont'd)

3. The waste is typically and frequently managed in non-oxidizing environments.

IV. Application of the Exclusion Rule to LTV's Roll Shop Wastes

The analytical data that follows confirms that the chromium present in the roll shop grinding process, grinder cooling water and roll shop wastes is exclusively (or nearly exclusively) trivalent chromium. Also included in this section is additional information showing how LTV manages the roll shop waste in a non-oxidizing environment.

Data is not available on the amount of hexavalent chromium present in the extract because all three laboratories had difficulty in performing the analysis. The laboratory problems included spike recoveries ranging from 0%-50% reported by the three labs, well below the 85% required to make the data viable. This problem was discussed with the USEPA's Technical Assessment Group. They replied that the three approved methods for hexavalent chromium analysis do not work well with sludges or any dirty matrix samples because many unknown interferences may hinder the detection of hexavalent chromium. To eliminate the interferences the laboratories diluted the samples, but that only increased the quantitation limit higher than the total concentration of chromium in the extract. Another explanation offered by the labs for their inability to detect hexavalent chromium in the waste extract is that since the amount of total

IV. Application of the Exclusion Rule to LTV's Roll Shop Wastes (cont'd)

chromium present in the extract is very low, the amount which is hexavalent is even lower. Hexavalent chromium is very difficult to detect at low concentrations.

There are three criteria in the above rule that must be met before the exclusion is granted

1. Part (6)(A)(i) requires that the chromium in the waste be exclusively or nearly exclusively trivalent chromium. The rule can be restated as saying that the chromium in the waste must not contain significant amounts of hexavalent chromium since the chief oxidation states of chromium are hexavalent and trivalent. Samples of each waste stream were submitted to three independent laboratories for analysis. The waste is first analyzed for total chromium and then for hexavalent chromium. The difference between the two values is the concentration of trivalent chromium in the waste.

   As is evident from Table 5, the percentage of hexavalent chromium present in each of the samples is minuscule. Of the nine samples analyzed, only one sample was reported to have chromium present in its hexavalent state at a concentration greater than 1% of the total amount of chromium. The average percent chromium in the waste present in its hexavalent state, depending upon the lab, varied from .00029% to 1.4%. Based upon these results, the chromium in the three waste streams is nearly exclusively trivalent and satisfies the first part of the toxicity characteristic chromium exclusion rule.

IV. Application of the Exclusion Rule to LTV's Roll Shop Wastes (cont'd)

2. The second part of the exclusion, Part (6)(A)(ii) requires that the waste be generated from an industrial process which uses trivalent chromium exclusively, and further requires that the process does not generate any hexavalent chromium. As evident from the process descriptions, there is no chromium used in the grinding process. Chromium is present in the alloy steel roll that is being ground. Chromium is added by the roll manufacturers as an alloy to improve hardenability, wear resistance and corrosion resistance. At no time during the grinding operation are any other sources of chromium present or introduced into the process.

To ascertain whether the metallic chromium in the grinder swarf is undergoing oxidation as a result of the grinding process, the swarf and the coolant from the three waste streams were analyzed for chromium and hexavalent chromium. Tables 5 and 6 show the amount of hexavalent chromium present in the sludge and in the coolant, respectively, as a result of the grinding operation. The percentage of hexavalent chromium in all three waste streams is very small. It should be noted that the waste coolants from all three roll shops are treated at NPDES permitted waste water treatment plants before being discharged. Based on the analysis performed by the three independent laboratories and the nature of the processes, none of the three roll shop waste streams use or generate hexavalent chromium.

IV. Application of the Exclusion Rule to LTV's Roll Shop Wastes (cont'd)

3. Part (6)(A)(iii) of the toxicity characteristic exclusion states that the waste be typically and frequently managed in non-oxidizing environments. To comply with this provision, it is first important to understand what kind of an environment is necessary for oxidizing chromium and then determine if such an environment exists at LTV's landfill.

The chromium in the sludge that is generated from the grinding operation at the three roll shops is either in its elemental state or in a metallic matrix with iron, carbon or other metals alloyed in the steel roll. Therefore, the chromium in the waste can be assumed to exhibit the physical properties common to metals. Chromium is used as an alloying material in steel because of its ability to resist air, water or other corrosive agents at ordinary temperatures, thus increasing its resistance to oxidation and corrosion. Chromium is also used as a coating for other metals because air renders it passive by forming a thin protective film on the metal's surface, and in this state, chromium is very resistive to chemical attack.

Metallic chromium is very difficult to solubilize or oxidize under ordinary conditions. A highly acidic environment and high temperatures are necessary to oxidize chromium. The solubility of chromium increases when exposed to pH levels below 3 or temperatures above 200°C, oxidizing it to either chromic acid

IV. Application of the Exclusion Rule to LTV's Roll Shop Wastes (cont'd)

(CrO_3), or chromic oxide (Cr_2O_3). The degree of oxidation is dependent upon the strength of the oxidizing agents. Chromium solubility in water is not a function of temperature. It is totally insoluble in water at any temperature. However, its solubility does increase with decreasing pH. Reagents that solubilize metallic chromium include the aqueous halogenic acids (e.g., HF, HBr, HCl, etc.) and sulfuric acid, H_2SO_4. Chromium solubility under strong basic conditions (pH above 12) is dependent upon temperature. Chromium is attacked by alkyl hydroxides but only when exposed to temperatures above 600-700°C. Strong bases (i.e., NaOH) do not attack chromium under ordinary conditions. Concentrated nitric acid (HNO_3) renders chromium passive. In its passive state, chromium does not dissolve in its ordinary reagents (e.g., H_2SO_4 or HCl).

In all samples that exhibited total chromium concentrations of 5 mg/l or higher, less than 1% of the total chromium in the sample went into solution when the wastes were analyzed for chromium via the EP toxicity test as tabulated in Table 5. In the EP toxicity test, which is used to simulate landfill conditions, the pH of the extract is maintained at 5.0. At this pH, it is difficult to solubilize metallic chromium. The data in Table 5 illustrates the aforementioned fact that conditions of high acidity are necessary to oxidize chromium, i.e., although chromium was present in the waste, very little went into solution.

IV. Application of the Exclusion Rule to LTV's Roll Shop Wastes (cont'd)

The aforementioned conditions constitute an oxidizing environment for metallic chromium, conditions which do not exist at LTV's landfill. The pH conditions at LTV's landfill do not approach the acidity necessary to oxidize chromium. For the eight waste streams permitted for disposal at LTV's landfill (see Table 7), the volume weighted average pH is 10.3. Given this, LTV's landfill does not meet the first criteria for an oxidizing environment for chromium. As stated previously, conditions of relatively high acidity are necessary to oxidize and solubilize metallic chromium. Based upon the waste characterization study (previously submitted to IDEM) performed by an independent concern on the eight waste streams deposited at the landfill, pH conditions at LTV's landfill are neutral or basic, thus decreasing the oxidation or solubility potential of the chromium in the waste streams. Furthermore, none of the reagents (the aqueous halogenic acids and H_2SO_4) necessary to oxidize metallic chromium are or will be present at LTV's landfill. The only halogenic acid waste generated by LTV, spent pickle liquor (used HCL), is processed off site for reuse. As far as the potential oxidizing of chromium when exposed to high temperatures is concerned, LTV's landfill is inorganic, as evident from the 8 waste streams listed in Table 7 that are landfilled at the facility. The only organic waste

IV. Application of the Exclusion Rule to LTV's Roll Shop Wastes (cont'd)

streams landfilled at the site, the tandem mill oily sludge, composes only 2.4% of the landfill. This is hardly enough organic material to raise the temperature above the 200°C mark necessary for oxidation to begin. Since no organic decay is occurring, the temperature at the landfill can never reach the greater than 200°C (>392°F) necessary to oxidize the chromium in the waste streams. Given the conditions for an oxidizing environment for chromium and their absence at LTV's landfill, LTV's roll shop waste meets the final criteria of the chromium toxicity exclusion rule.

V. Summary

IDEM personnel requested that LTV Steel submit information to support LTV's claim that the roll shop waste was excluded from hazardous waste regulation.

LTV performed a study on the chromium content of materials involved at the roll shop and researched the oxidation of chromium in general. The data collected indicates that the chromium content in the waste is nearly exclusively trivalent chromium. The process description as well as the data collected confirms that the process uses nearly exclusively trivalent chromium and that the process does not generate hexavalent chromium. An oxidizing environment for chromium was discussed and shown not to

V. Summary (cont'd)

exist at LTV Steel's on-site solid waste disposal facility. Therefore, the three criteria necessary for a chrome bearing waste to be excluded from hazardous waste regulation have been met.

VI. Tables

Table 1: Typical Chem. Analysis of the Rolls at the 84" Hot Strip Mill
(% by weight)

Type	# of rolls	C	Cr	Mn	Mo	Ni	P	Si	S
Alloy Steel	178	3.2	1.5	0.81	0.32	4.49	0.11	0.92	0.05
High Cr Alloy Steel	72	2.69	16.0	1.00	1.16	1.01	0.035	0.81	0.032

VI. Tables (cont'd)

Table 2: Chemical Analysis of a Typical Alloy Steel Roll at No. 3 Sheet Mill
(% by weight)

C	Cr	Mn	Mo	P	Si	S	V
0.77	2.50	0.31	0.20	0.01	0.24	0.006	0.062

Table 3: Typical Chem. Analysis of the 4 High Percentage Cr Rolls at No. 3 Sheet Mill
(% by weight)

C	Cr	Mn	Mo	Ni	P	Si	S
2.85	17.36	0.87	1.88	0.92	0.03	0.84	0.02

VI. Tables (cont'd)

Table 4: Chem. Analysis of a Typical Alloy Steel Roll at No. 2 Tin Mill
(% by weight)

C	Cr	Mn	Mo	Ni	P	Si	S
0.86	2.34	0.31	0.18	0.14	0.009	0.250	0.009

VI. Tables (cont'd)

Table 5: Analysis of Roll Shop Sludges

84" Hot Strip Mill Roll Shop Sludge

Parameter	Atec	Net	Quality
Total Cr (ppm)	14000	3.9	1430
Hex. Cr (ppm)	< 0.02**	< 0.001**	9.6
% Hex. Cr*	0.00014	0.026	0.67
EP Tox Cr (ppm)	2.2	< 0.04	1.5

No. 3 Sheet Mill Roll Shop Sludge

Parameter	Atec	Net	Quality
Total Cr (ppm)	7600	3.3	1310
Hex. Cr (ppm)	0.03	< 0.01	12
% Hex. Cr*	0.00039	0.30	0.92
EP Tox Cr (ppm)	7.5	1.5	0.3

No. 2 Tin Mill Roll Shop Sludge

Parameter	Atec	Net	Quality
Total Cr (ppm)	5800	1.6	1110
Hex. Cr (ppm)	< 0.02**	< 0.01	29
% Hex. Cr*	0.00034	0.63	2.6
EP Tox Cr (ppm)	< 0.5	0.61	4.2

	Atec	Net	Quality
Avg. % Hex Cr	0.00029	0.32	1.4

* Percentage of chromium in the waste as hexavalent chromium.

** Below Quantitation Limit.

VI. Tables (cont'd)

Table 6: Analysis of Roll Shop Waste Coolant

84" Hot Strip Mill Roll Shop

Parameter	Atec	Net	Quality
Total Cr (ppm)	1.6	0.04	1.5
Hex. Cr (ppm)	< 0.02*	< 1.0**	< 0.1*

No. 3 Sheet Mill Roll Shop

Parameter	Atec	Net	Quality
Total Cr (ppm)	1.6	0.95	0.3
Hex. Cr (ppm)	0.9	< 1.0**	< 0.1*

No. 2 Tin Mill Roll Shop

Parameter	Atec	Net	Quality
Total Cr (ppm)	22.0	0.15	0.2
Hex. Cr (ppm)	0.06	< 1.0**	< 0.1*

* Below quantitation limit.

** Sample diluted to eliminate interferences thus causing high quantitation limits.

VI. Tables (cont'd)

Table 7: pH Values of the Eight Landfilled Waste Streams

	Waste Stream	Generation Rate (yd^3/yr)	pH
1.	BOF Precipitator Dust	62,000	11.0
2.	Terminal Lagoon Sludge	20,000	8.0
3.	Reladle/Desulfurization Baghouse Dust	6,800	11.0
4.	MSD Filter Plant Sludge	4,500	9.3
5.	Tandem Mill Oily Sludge	2,400	6.9
6.	Caster Scale Pit Sludge	2,000	6.9
7.	Roll Shop Wastes	1,000	8.6
8.	LMF Baghouse Dust	100	11.0

Volume weighted average pH = 10.3

VII. References

1. Calovini, Frank, United States Environmental Protection Agency, Technical Assessment Group

2. Considine, Douglas M., Van Nostrand's Scientific Encyclopedia, Van Nostrand Reinhold Co., 5th Edition, Pg. 545-547

3. Lange, Norbert Adolph, Handbook of Chemistry, Handbook Publishers, Inc. 1952, 8th Edition, Pg. 225-225

4. Leighor, Robert B., Chemistry of Engineering Materials, Mc Graw Hill, 4th Edition, 1942, Pg. 185-188

5. Lowenheim, Frederick, Electroplating: Principles and Practice, Mc Graw Hill, 1978, Pg. 226-229

6. Wharpe, A.G., Inorganic Chemistry, Longman Scientific and Technical, 2nd Edition, Pg. 583-588

7. White, Paul, SAIC - contracted by the Unites States Environmental Protection Agency, Technical Assessment Group to handle SW846 Methodology questions.

VIII. Laboratory Data

REPORT OF TEST RESULTS

Client: LTV Steel

Sample Matrix: Sludge
Sample Taken By: Client
Date Sampled: February 11, 1991
Date Received: February 11, 1991
ATEC Lab Number: 910082
ATEC Project Number: 52-08040

PARAMTER (unit in mg/L unless noted)	SAMPLE I.D. NUMBER 3 S.M. SLUDGE	2 T.M. SLUDGE	84"H.S.M. SLUDGE	QUANTI-TATION LIMIT	SW 846 METHOD NO.
EPTOX Chromium	7.5	<0.5	2.2	0.5	6010
Total Chromium (mg/kg)	7600	5800	14000	5.0 mg/kg	6010

Respectfully submitted,
ATEC Associates, Inc.

Elizabeth Brown
Environmental/Analytical
Testing Division

REPORT OF TEST RESULTS

Client: LTV Steel

Sample Matrix: Water
Sample Taken By: Client
Date Sampled: February 11, 1991
Date Received: February 11, 1991
ATEC Lab Number: 910082
ATEC Project Number: 52-08040

PARAMTER (unit in mg/L unless noted)	SAMPLE I.D. NUMBER 3 S.M. H2O	2 T.M. H2O	84"H.S.M. H2O	QUANTI-TATION LIMIT	SW 846 METHOD NO.
Total Chromium	1.6	22	1.6	0.5	6010

Respectfully submitted,
ATEC Associates, Inc.

Elizabeth Brown
Environmental/Analytical
Testing Division

REPORT OF TEST RESULTS

Client: LTV Steel

Sample Matrix: Water
Sample Taken By: Client
Date Sampled: February 11, 1991
Date Received: February 11, 1991
ATEC Lab Number: 910082
ATEC Project Number: 52-08040

PARAMTER (unit in mg/L unless noted)	SAMPLE I.D. NUMBER 3 S.M. H2O	2 T.M. H2O	84"H.S.M. H2O	QUANTI-TATION LIMIT	SW 846 METHOD NO.
Hexavalent Chromium	0.9	0.06	<0.02	0.02	7196

Respectfully submitted,
ATEC Associates, Inc.

Elizabeth Brown
Environmental/Analytical
Testing Division

REPORT OF TEST RESULTS

Client: LTV Steel

Sample Matrix: Sludge
Sample Taken By: Client
Date Sampled: February 11, 1991
Date Received: February 11, 1991
ATEC Lab Number: 910082
ATEC Project Number: 52-08040

NEUTRAL LEACHATE PARAMTER (unit in mg/L unless noted)	SAMPLE I.D. NUMBER 3 S.M. SLUDGE	2 T.M. SLUDGE	84"H.S.M. SLUDGE	QUANTI-TATION LIMIT	SW 846 METHOD NO.
Hexavalent Chromium	0.03	<0.02	<0.02	0.02	7196

Respectfully submitted,
ATEC Associates, Inc.

Elizabeth Brown

Environmental/Analytical
Testing Division

INORGANIC
QUALITY CONTROL SUMMARY

MATRIX: WATER SOIL SLUDGE OTHER_____

PERCENT SOLIDS:_____ DRY WEIGHT [ ] AS RECEIVED [✓]

TEST	DIGESTION/ PREP DATE	ANALYSIS DATE	QUANT. LIMIT	METHOD BLANK	METHOD STANDARD	T.V.	% REC.	SAMPLE I.D.	SAMPLE RESULT	DUPLICATE RESULT	% RSD	SPIKE RESULT	SPIKE T.V.	% REC.
Cr	2-18-91	2-26-91	0.05	<0.05	0.195	0.20	98							
Cr	2-19-91	2-26-91	0.05	<0.05	0.197	0.20	99	082-1	7500mg/kg	7200mg/kg	Not Applicable *			
Cr	2-18-91	3-1-91	0.05	<0.05	0.185	0.20	93	084-4	<0.05	<0.05	NA	0.212	0.20	105
NEUTRAL LEACHATE														
Cr	2-18-91	2-26-91	0.05					082-1N	0.001	--	--	1.05	1.00	105
Cr	2-18-91	2-26-91	0.05					082-2N	0.003	--	--	1.04	1.00	104
Cr	2-18-91	2-26-91	0.05					082-3N	-0.005	--	--	1.06	1.00	106

* NO SPIKE RECOVERY REPORTED DUE TO HIGH ANALYTE RECOVERY

INORGANIC
QUALITY CONTROL SUMMARY

MATRIX: WATER SOIL SLUDGE OTHER_____

PERCENT SOLIDS:_____ DRY WEIGHT [ ] AS RECEIVED [ ]

TEST	EXTRACTION DIGESTION/ PREP DATE	ANALYSIS DATE	QUANT. LIMIT	METHOD BLANK	METHOD STANDARD	T.V.	% REC.	SAMPLE I.D.	SAMPLE RESULT	DUPLICATE RESULT	% RSD	SPIKE RESULT	SPIKE T.V.	% REC.
NEUTRAL LEACHATE ON SLUDGE														
Cr+6	2-12-91	2-13-91	0.02	<0.02	0.495	0.5	99	082-1N	0.027	0.027	0	0.456	0.5	86
Cr+6	2-12-91	2-13-91	0.02					082-2N	<0.02	<0.02	NA	0.495	0.5	99
Cr+6	2-12-91	2-13-91	0.02					082-3N	<0.02	<0.02	NA	0.495	0.5	99
WATER ANALYSIS														
Cr+6		2-11-91	0.02	<0.02	0.495	0.5	99	082-4	0.90			1.07	0.17	100
Cr+6		2-11-91	0.02					082-5	0.06			0.15	0.1	90
Cr+6		2-11-91	0.02					082-6	<0.02	<0.02	NA	0.495	0.5	99

NATIONAL ENVIRONMENTAL TESTING, INC.

NET Midwest, Inc.
Indianapolis Division
6984 Hillsdale Court
Indianapolis, IN 46250
Tel: (317) 842-4281
Fax: (317) 842-4286

ANALYTICAL REPORT

Mr. Mohammad Babar
LTV STEEL
3001 Dicky Road
East Chicago, IN 46312

04-09-91

P.O. NO.: 308146

Date Received: 03-26-91

Sample Number/ Parameters	Sample I.D.	Results	Sample Date/ Units
36412	84 HOT STRIP MILL ROLL SHOP SLUDGE		03-25-91
Chromium, Hexavalent		<1.0	ug/g
Chromium, Total		3900.	ug/g
EP Tox - Chromium		<0.04	mg/L
EP Tox - Chromium, Hex.		<1.0	mg/L
36413	#2 TIN MILL ROLL SHOP SLUDGE		03-25-91
Chromium, Hexavalent		<10.	ug/g
Chromium, Total		1600.	ug/g
EP Tox - Chromium		0.61	mg/L
EP Tox - Chromium, Hex.		<10.	mg/L
36414	#3 SHEET MILL ROLL SHOP SLUDGE		03-25-91
Chromium, Hexavalent		<10.	ug/g
Chromium, Total		3300.	ug/g
EP Tox - Chromium		1.5	mg/L
EP Tox - Chromium, Hex.		<10.	mg/L

Karen Groleau

Karen Groleau
Project Manager