Hexavalent Chromium Risks for Fossil and CCGT Plants
Sources, Sinks, and Risk Management (plus chemistry)

HRSG Forum Virtual Training 2021

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Includes technical information from
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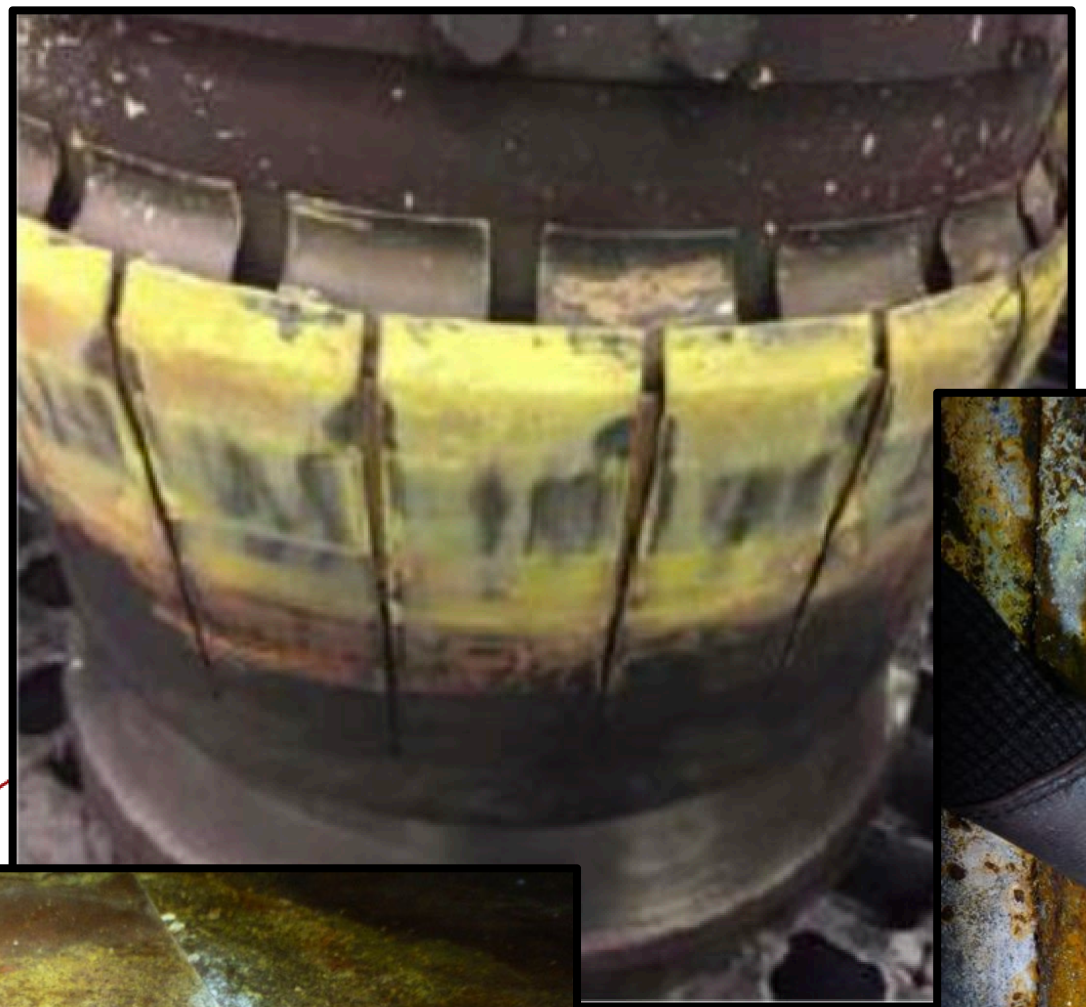

Presentation Outline

1. Introduction
2. Chromium and hexavalent chromium
3. Hexavalent chromium toxicity
4. Gas turbines/steam turbines/steam pipes/HRSG
5. Testing
6. Formation chemistry
7. Risk management
8. Removal/Decontamination
9. Plant risk areas
10. Summary

Thermal Chemistry - Key Technical Services

Thermal Chemistry is a specialist chemistry consulting company providing independent chemistry, materials, environmental and hazard & risk management related services to the thermal and geothermal power and CoGeneration industries in New Zealand and internationally.

Experience – David Addison

- **Over 24 years experience in the power industry**
  - BSc(Tech) – Chemistry
  - MSc(Tech) – Materials Science/Flow-accelerated Corrosion

- 1997 to 2008 - 12 years in the chemistry group with the Electricity Corporation of New Zealand and then Genesis Energy as a Senior Projects Chemist.
  - Conventional coal and gas units, open cycle gas turbines and combined cycle gas turbines

- Thermal Chemistry Limited since April 2008 as Principal Consultant
  - Work worldwide (but based from New Zealand), thermal, geothermal, cogeneration plants
  - Reviews/audits/troubleshooting/training/inspections/commissioning/new project specification etc

Experience – David Addison

- Member of the International Association for the Properties of Water and Steam (IAPWS) – www.iapws.org
  - Leading international organization for the thermophysical properties of water and steam
  - IAPWS Power Cycle Chemistry (PCC) Vice Chairperson – heavily involved in the development of power plant cycle chemistry guidance documents for industry (free to download)

- International Advisory Board (IAB) member – PPChem Journal

- Chairperson New Zealand Association for the Properties of Water and Steam (NZAPWS) – www.nzapws.org

- Consultant and Author, guideline development - Electrical Power Research Institute (EPRI) – www.epri.com

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Chromium and Hexavalent Chromium

- Chromium common alloy element – stainless steels and high chromium containing materials. Present in
  - Steam turbines
  - Gas turbines
  - Boilers
  - HRSGs

- Transition metal
- Multiple oxidation states
- Chromium III (3+) essential for human health (trivalent chromium) in small amounts
- Stainless steel has oxide of chromium(III) oxide on surface – normal product of passivation and corrosion
- Chromium VI (6+) solids extremely toxic (Hexavalent chromium) – often “brightly colored” – (yellow)

Hexavalent Chromium

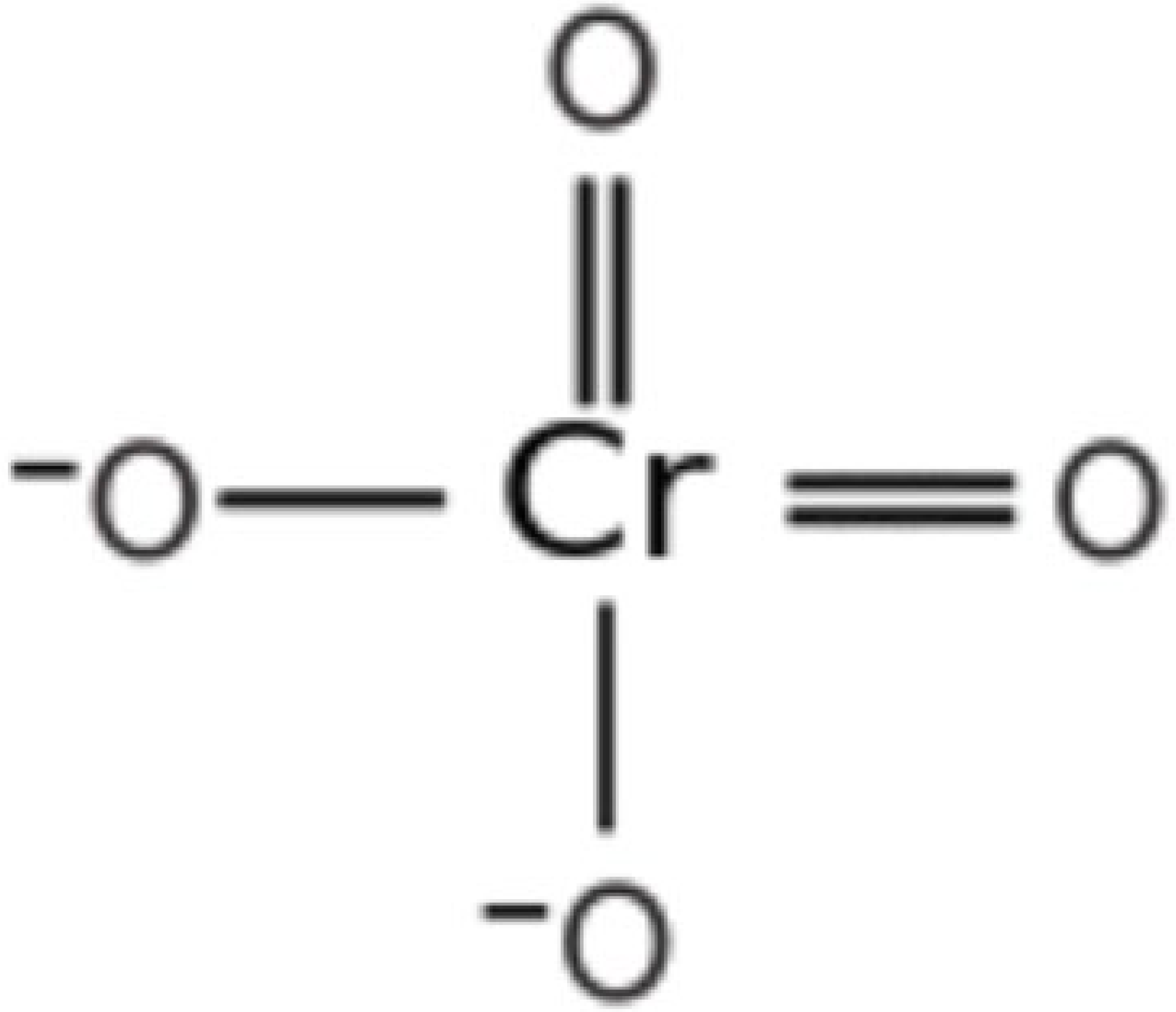
- Hexavalent chromium is bonded with oxygen (two double bonds and two single bonds) and will pair with mono or divalent cations via the single bonded oxygen but the chromium is the VI (6+) oxidation state e.g.

- Na_2CrO_4 – Sodium chromate
- $CaCrO_4$ – Calcium chromate
- K_2CrO_4 – Potassium chromate

- Often also as a dihydrate with additional water of crystallization present

- Used as industrial dye, leather tanning, wood preservation, anti corrosion coating etc and formed from stainless steel welding/plasma cutting etc

- Also in tobacco smoke



Hexavalent Chromium Toxicity

- Carcinogen;
  - Inhalation (breathing) - fumes or aerosols – increased rates of lung cancer
  - Ingested (eating/mucus membranes) – eyes, nose, mouth – can cause permanent eye damage
  - Dermal absorption (skin) – “chrome ulcers” + contact dermatitis

- Inhalation of Cr(VI) particulates can also cause
  - Chronic respiratory irritation
  - Chronic bronchitis
  - Emphysema
    - “Welders Cough”

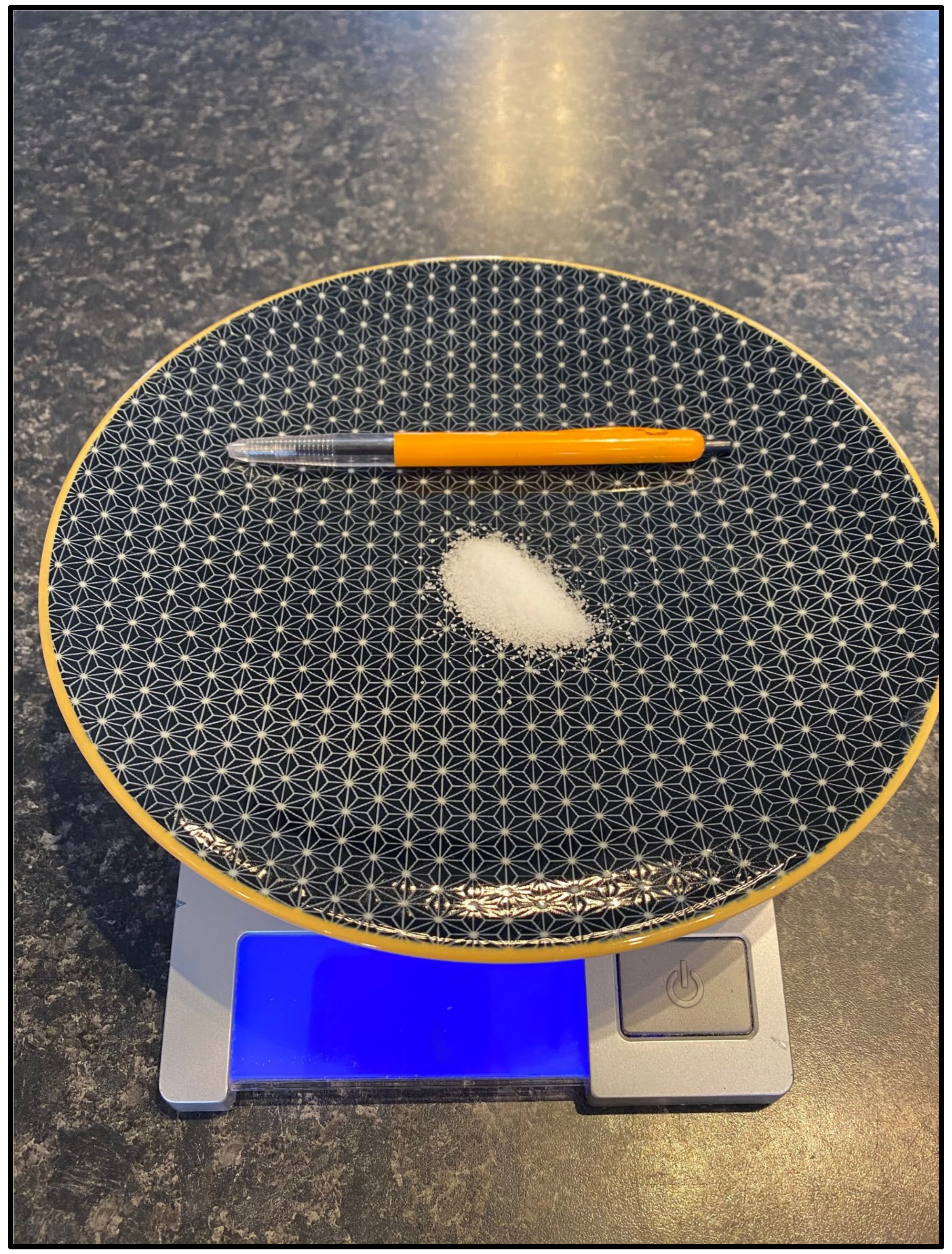
- OSHA & similar permissible exposure limits examples for calcium chromate (100% solution)
  - **Inhalation** – 8 hours at 0.05 mg/m^3
  - **Dermal** – 10% of body surface exposure has been reported as fatal
  - **Ingestion** – ~0.5 g can result in serious toxicity
  - **Median Lethal dose** – 50-150 mg/kg of body weight

- Easily managed risks with standard industrial hygiene and PPE strategies applied combined with neutralization where needed

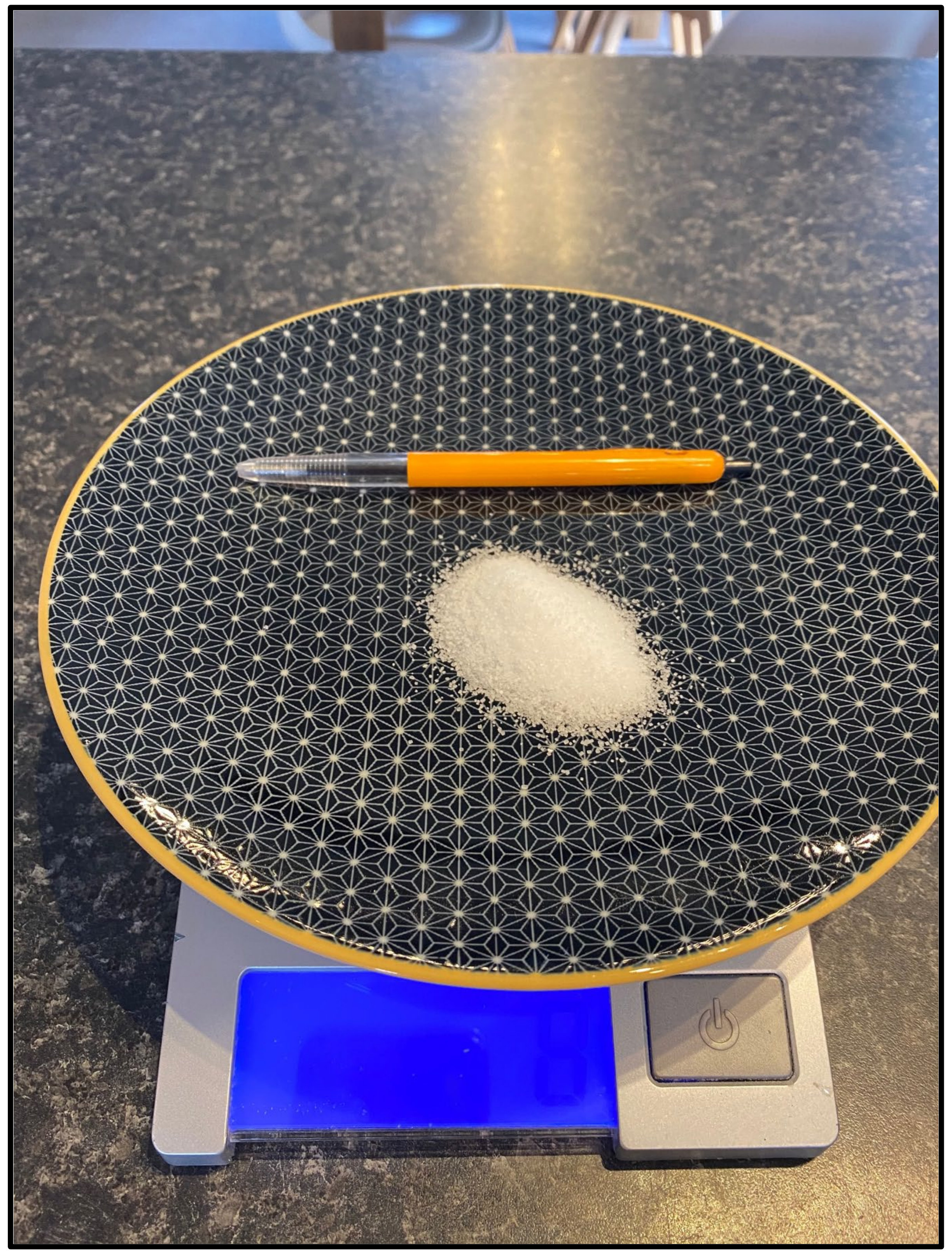
- Exposure can be detected by urine testing – pre and post testing – limit of concern is 5 µg/L. A change pre/post shift of more than 10 µg/L or 25 µg/L at end of work week indication of excessive exposure. ½ life is 15-41 hours post exposure. Levels relate to 8 hours at 0.05 mg/m^3 exposure limit

Toxic Dose Approximate Volumes Examples

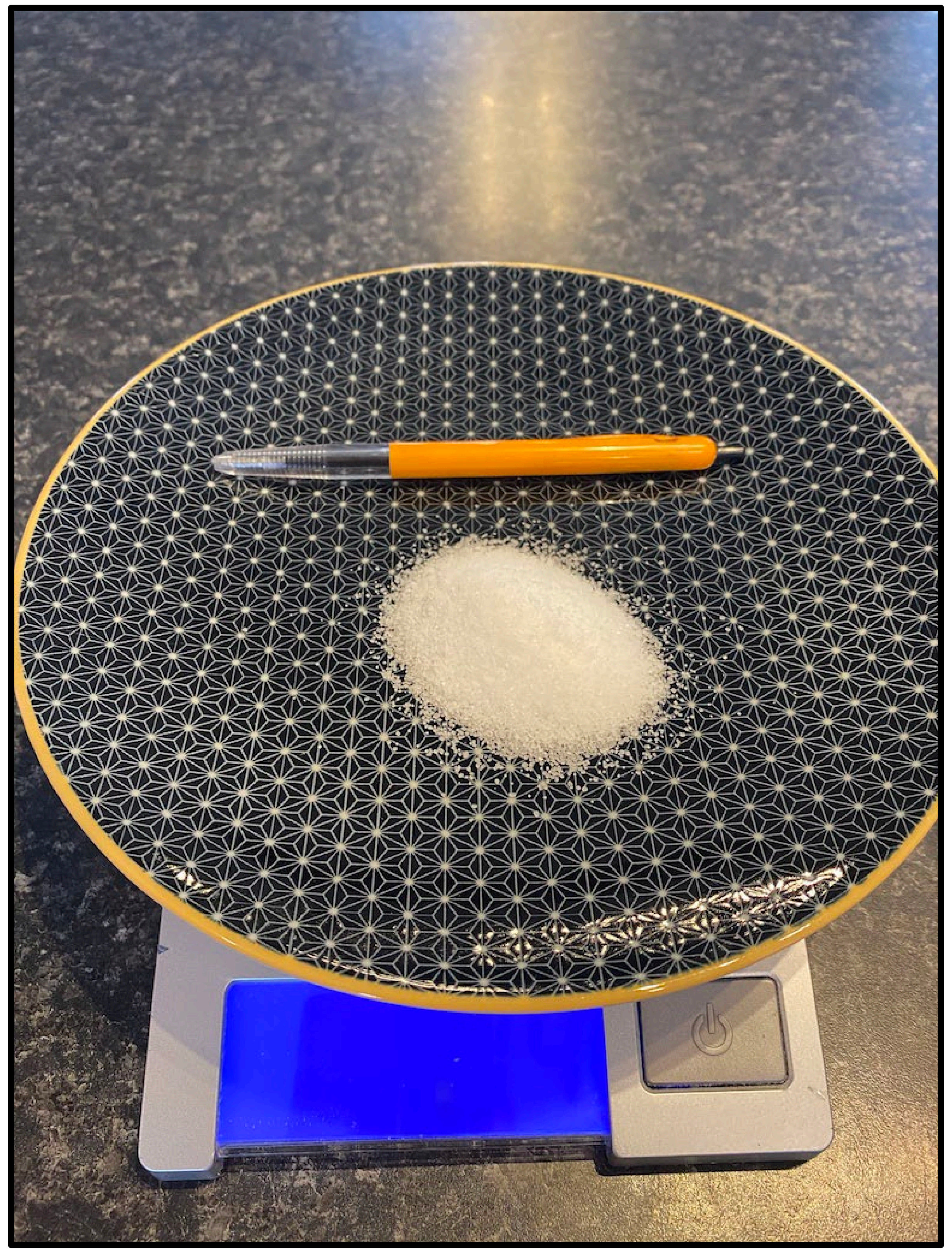
0.85 g 30% $CaCrO_4$



8 g 100% $CaCrO_4$



14 g 30% $CaCrO_4$



Hexavalent Chromium

- Risk associated with welding of high chromium materials well understood in industry

- Under high temp/energy welding hexavalent chromium fumes (chromium (VI) trioxide, CrO_3) produced under welding conditions

- Risks managed by
  - Area ventilation – welding booths
  - Masks/Supplied Air
  - Skin protection
  - Personal monitoring

- Can be present in boiler/HRSG chemical cleaning waste as well – depends on clean chemistry. Well understood and managed as part of chemical clean procedures

Gas Turbines/Steam Turbines/HRSGs

- Recently hexavalent chromium identified as yellow deposits (but not full ionic structure reported) on
  - Gas turbine hot gas path components
  - Steam turbine hot external components - bolts
  - HRSG/Boiler hot pipe external surfaces
- Limited scientific literature available in relation to GT/ST/HRSG and chromium (VI)
- Safety notices issued by GT/ST OEMs (GE and Siemens) and some plant owner/operators
- For GT/ST link made to calcium containing anti-size pastes used on hot components – advised to avoid these products
- Can be tested for in the field via 3M or similar test field test kits – fast screening tool
- May have been historically misidentified as sulfur deposits in HRSGs from fuel (also yellow but thermodynamically impossible to be present)

Literature and OEM References

Journal of the Ceramic Society of Japan 123 [8] 677-684 2015 Paper

The formation of Cr(VI) compound at the interface between metal and heat-insulating material and the approach to prevent the formation by sol–gel process

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Oxid Met (2012) 78:83–102
DOI 10.1007/s11085-012-9293-7

ORIGINAL PAPER

Alkali Induced High Temperature Corrosion of Stainless Steel: The Influence of NaCl, KCl and $CaCl_2$

S. Karlsson · J. Pettersson · L. -G. Johansson · J. -E. Svensson

Received: 8 July 2011 / Revised: 9 March 2012 / Published online: 27 April 2012

GE Power

Product Service

Hexavalent chromium residue on steam turbine components

Publish Date: 02 DECEMBER 2019

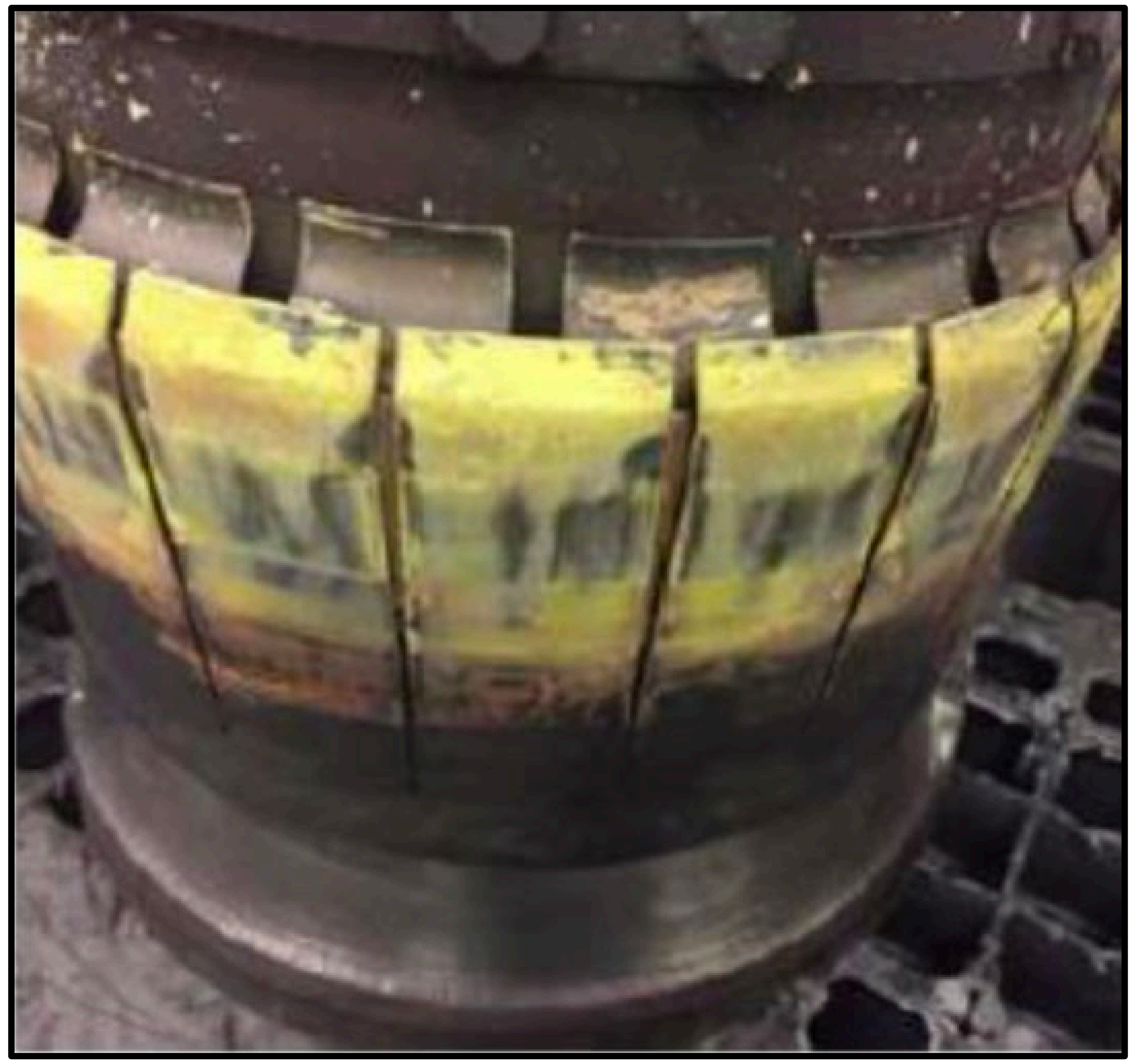
KB0027253

Safety Bulletin

Overview

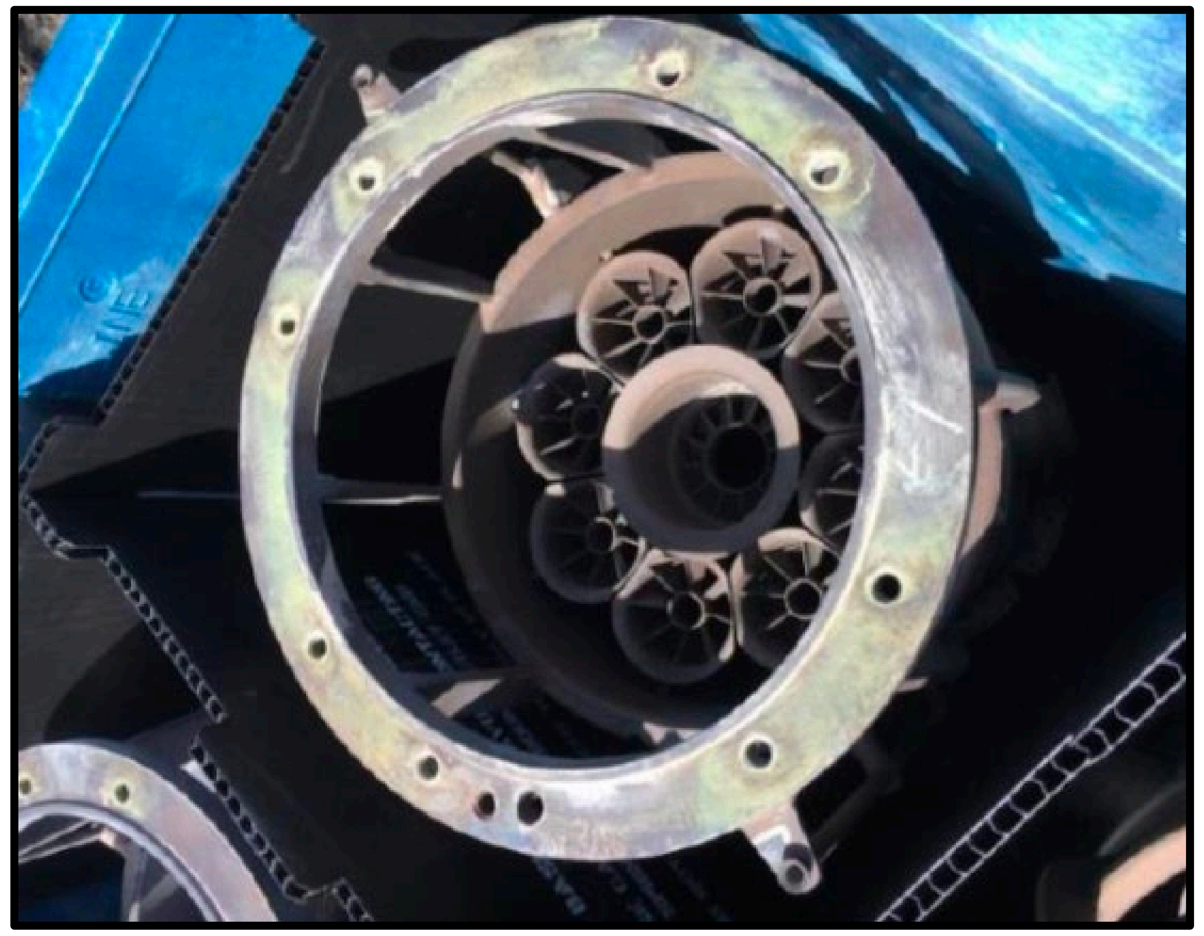
To inform of a potential contaminant accumulation (yellow or white residue) on steam turbine, steam generator and water-steam-cycle hardware occurring where certain anti-seize compounds are applied to Chromium-containing metals and exposed to elevated temperatures (above 400°C). This bulletin contains recommended safety precautions and risk mitigations.

Gas Turbines



GT Combustor Basket Spring Clips

Rotor Bolts



GT Combustor Basket Flange

Steam Pipes

RH Bypass

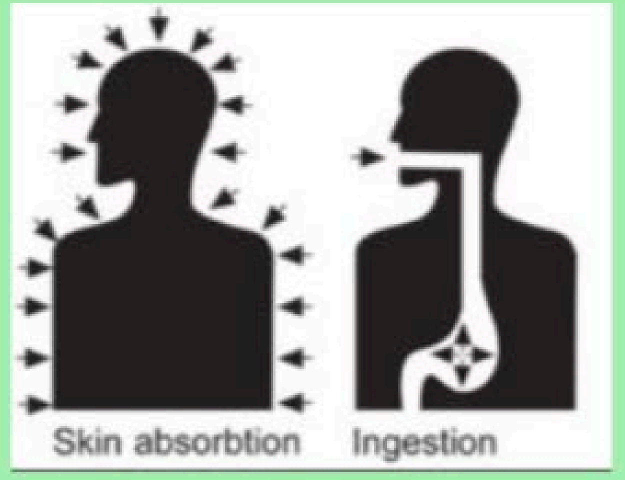
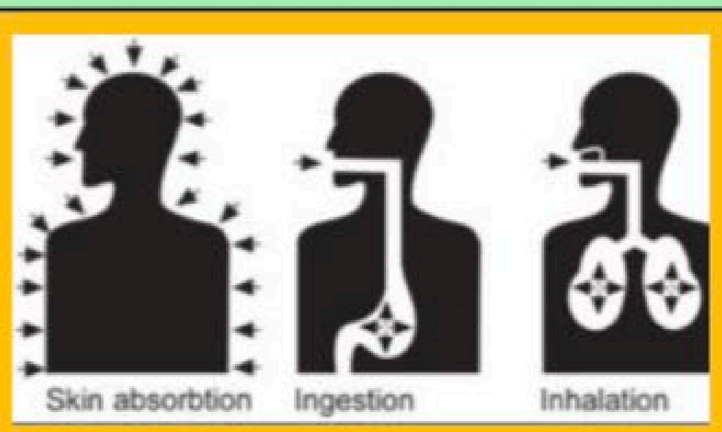
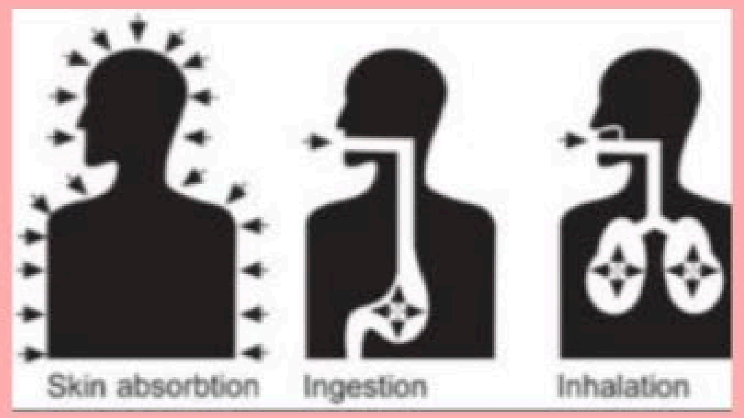
HRSG Internal Surfaces – Access Doors

Hexavalent Chromium Safety Precautions - Example

Recommendations

Now that a positive swab has identified Hexavalent Chromium the following controls must be in place relevant to the activity being undertaken in this area of the plant:

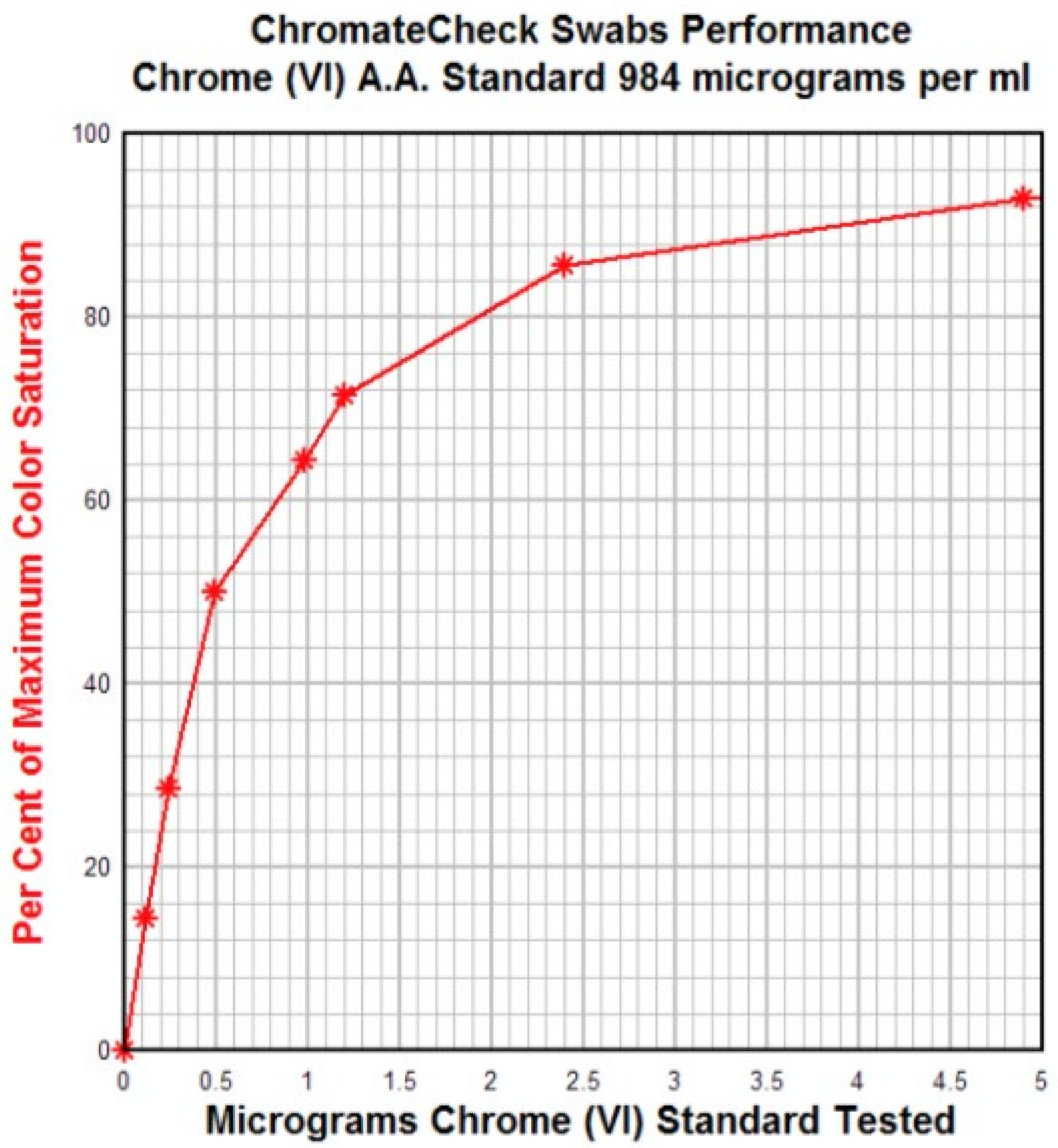
Note: Products such as WD-40 or Kroil Oil can be used to dampen CrVI affected areas.

Activity	Exposure	Controls
Inspections in areas where CrVI residues are present. **(No residue disturbance)**		Eye Protection Disposable nitrile gloves Particle resistant disposable overalls. No eating, drinking, smoking, or bathroom breaks should be taken without first washing hands and face.
Assembly, removal or disassembly of items with CrVI residues present.		As above with: P2 respirator Where possible (as required) consider ultrasonic cleaning of parts.
Grinding, wire brushing, linishing, welding etc of CrVI confirmed residues.		As above with: Goggles Respiratory Protection: upgrade to powered air purifying respiratory protection. Mechanical ventilation HEPA filters Controls to limit the aerosolisation of CrVi residues **MUST** be applied.

3M Chromate Test Kit – Field Screening

- VERY Sensitive field test – color change
- Reported detection limit ~ 0.037 µg/L (ppb) – very, very low
- Only detects chromium (VI) not chromium (III)
- Diphenylcarbohydrazide colour change reaction

3M Chromate Test Kit – Field Screening



The following table illustrates the reaction of ChromateCheck™ Swabs to each concentration.

Chromate Tested (μg)	Color Result	Rating (%)
9.8	Deep purple	100
4.9	Deep Purple	93
2.4	Purple	86
1.2	Purple	71
0.98	Medium to dark purple	64
0.49	Medium to dark purple	50
0.24	Light purple	28
0.12	Light purple - easily seen	14
0 (no Cr (VI))	Colorless	0

Legend

Standard curves were developed using several lots of the new version of ChromateCheck™ Swabs. A standard solution of 984 micrograms/ml chromate was diluted to produce the concentrations used in each series of experiments. The results of several curves were averaged and have been summarized in the above graph. The intensity of the purple/pink color developed at each of the concentrations was scored as a percentage of the maximum color developed.

Other Analysis Methods

- Other diphenylcarbohydrazide colour change methods/test kits – field screening and lab testing
- X-Ray Fluorescence (XRF) analysis of powdered samples for elemental only analysis
- X-Ray Diffraction (XRD) analysis of powdered samples for compound analysis – oxidation state able to be determined
- XRF/XRD ~1% detection limit

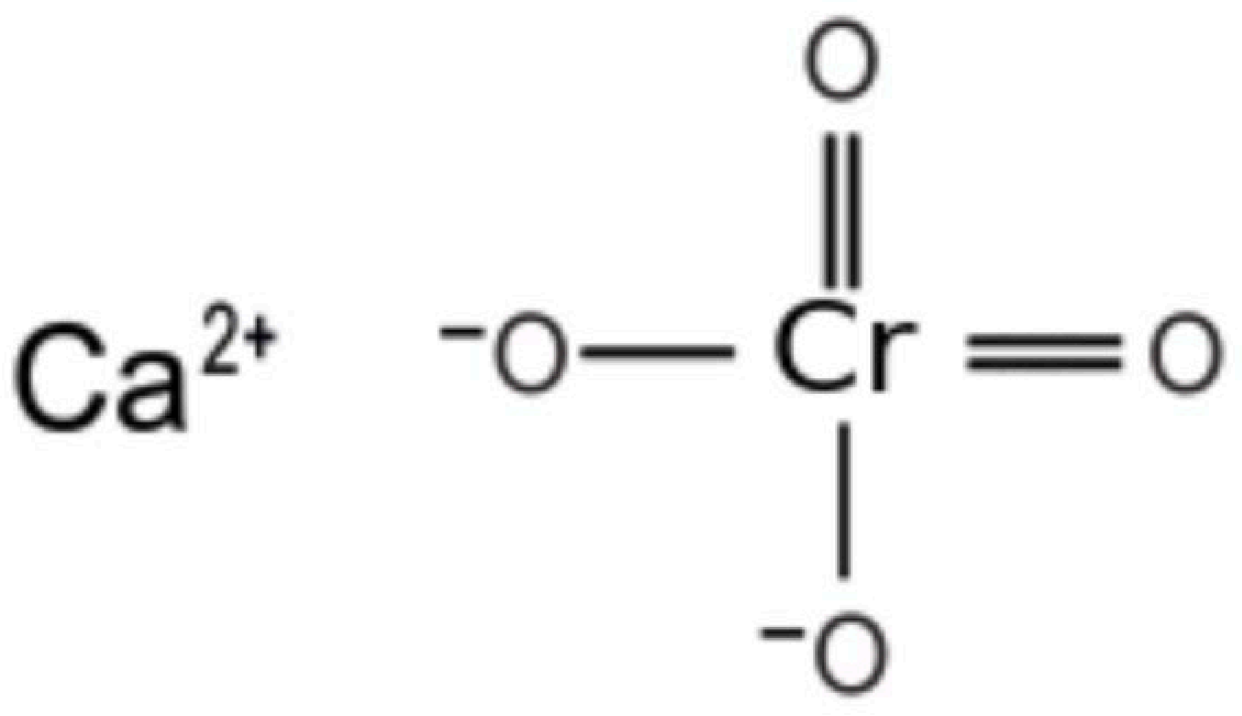
What is Going On Chemically?

- To get Hexavalent Chromium you need the following

1. A chromium containing material (will not occur with carbon steel)
2. A high temperature environment (in excess of 150-200 °C/200-400+ °F)
3. An oxidizing environment (%’s oxygen required, not ppb’s)
4. Chromium (III) oxide
   – Oxidation of a chromium containing material or
   – Corrosion of a chromium containing material
5. For a solid deposit (more to follow on this) you also need a specific salt/cation as a counter ion to balance the reaction – most commonly calcium ions

Will not occur on internal water/steam touched surfaces. Gas pass or hot external surfaces only under certain, specific conditions

Hexavalent Chromium Form

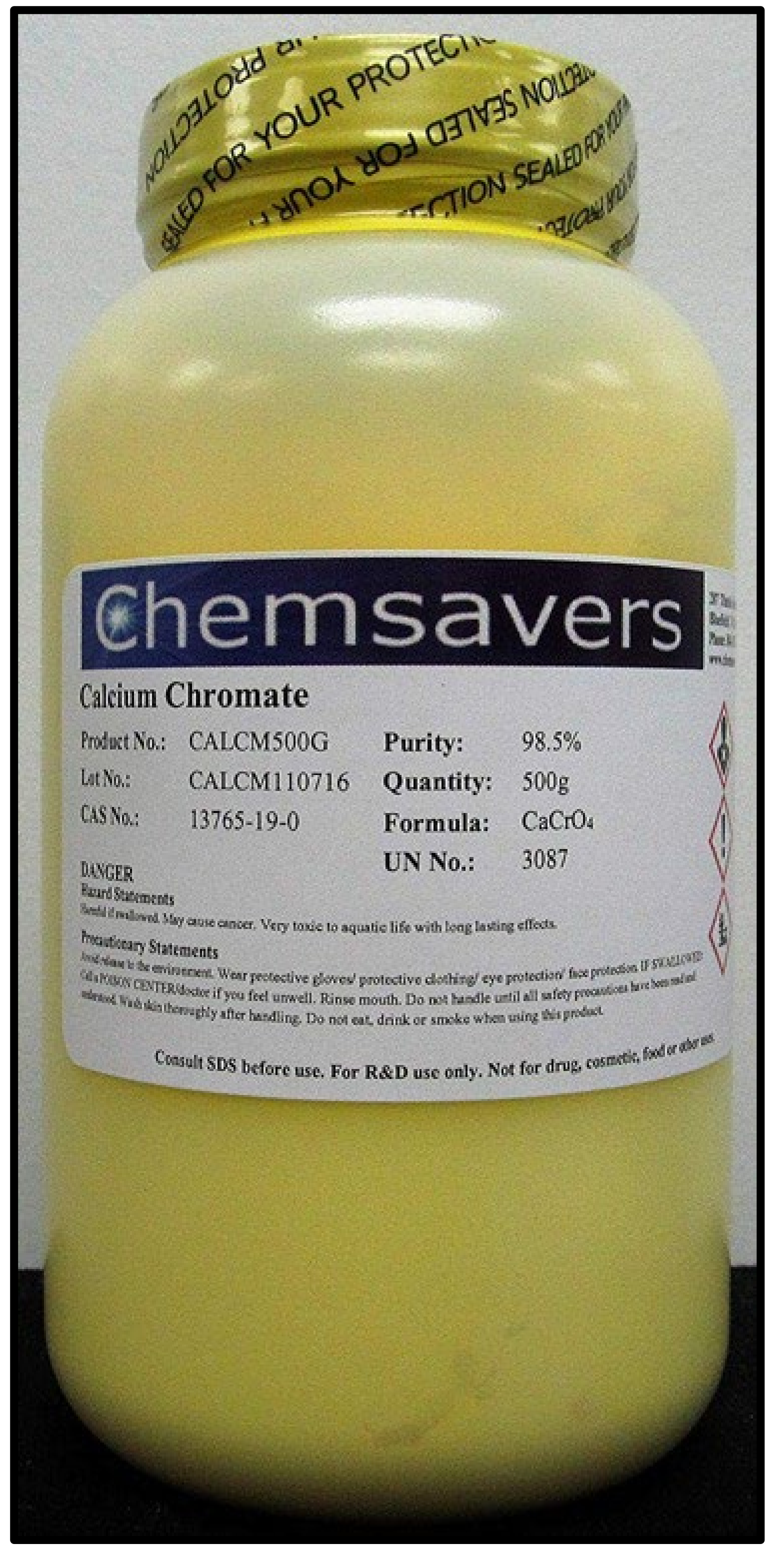


Calcium chromate

- OEM safety bulletins does not specify what chemical form the Hexavalent Chromium is in but literature references calcium salts

- Thermal Chemistry XRD/XRF testing however for HRSG casing deposits has confirmed form as Calcium Chromate or $CaCrO_4$ – Yellow color

- GT/ST/Steam Pipe examples expected to also be calcium chromate based on expected chemistry and physical appearance.



HRSG Internal Surfaces – Access Doors – Stainless Steel Liner Plates/Doors Only

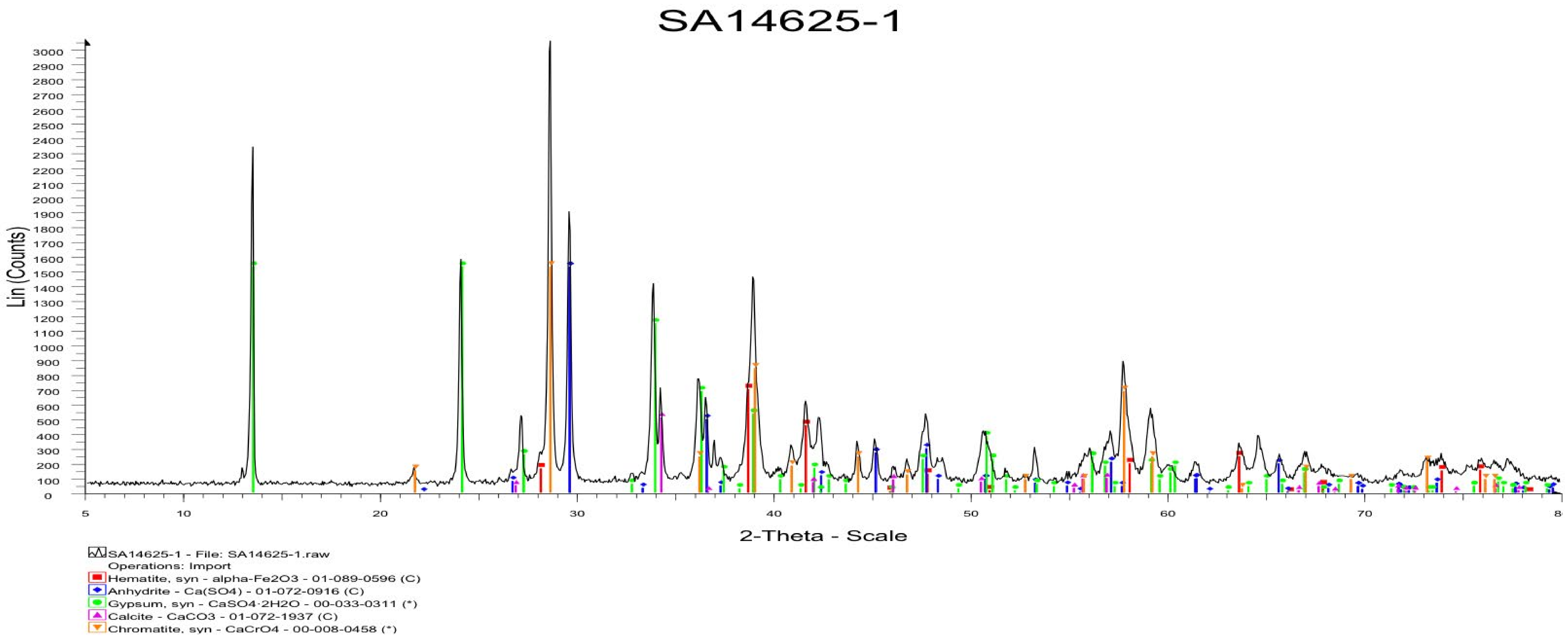
HRSG Casing Deposit Analysis

SPECTRACHEM ANALYTICAL

CRL Energy Ltd

SA14625 : Sample - "Lower gas pass door Deposit"

Phase Name	Phase Formula	Presence(%)
Gypsum	$CaSO_4 \cdot 2H_2O$	31
Chromatite	$CaCrO_4$	29
Anhydrite	$Ca(SO_4)$	19
Calcite	$CaCO_3$	15
Hematite	Fe_2O_3	7



Calcium Chromate – 29% + other calcium containing salts

Chromium Corrosion Products

SPECTRACHEM ANALYTICAL

CRL Energy Ltd

X-ray fluorescence
Spectra plus
Multi-element Analysis

CLIENT	:	**THERMAL CHEMISTRY LTD**
PROJECT	:	SA14625
DATE	:	12/12/11
SAMPLE	:	**"Lower gas pass door Deposit"**
COMMENTS	:	100% - Total = sum of unmeasured elements [H ->O]
	:	
	:	

Carbon	C	_	Zinc	Zn	0.072	Iodine	I	nd
Fluorine	F	nd	Gallium	Ga	nd	Caesium	Cs	nd
Sodium	Na	0.354	Germanium	Ge	nd	Barium	Ba	nd
Magnesium	Mg	0.410	Arsenic	As	nd	Lanthanum	La	nd
Aluminium	Al	0.049	Selenium	Se	nd	Cerium	Ce	_
Silicon	Si	0.148	Bromine	Br	nd	Hafnium	Hf	_
Phosphorus	P	nd	Rubidium	Rb	nd	Tantalum	Ta	nd
Sulphur	S	12.4	Strontium	Sr	0.031	Tungsten	W	nd
Chlorine	Cl	0.874	Yttrium	Y	nd	Rhenium	Re	_
Potassium	K	0.109	Zirconium	Zr	0.003	Osmium	Os	_
Calcium	Ca	22.3	Niobium	Nb	nd	Iridium	Ir	_
Scandium	Sc	nd	Molybdenum	Mo	nd	Platinum	Pt	_
Titanium	Ti	0.009	Rhodium	Rh	_	Gold	Au	_
Vanadium	V	nd	Palladium	Pd	_	Mercury	Hg	nd
Chromium	Cr	14.0	Silver	Ag	_	Thallium	Tl	nd
Manganese	Mn	nd	Cadmium	Cd	nd	Lead	Pb	nd
Iron	Fe	10.0	Indium	In	_	Bismuth	Bi	nd
Cobalt	Co	nd	Tin	Sn	nd	Thorium	Th	nd
Nickel	Ni	0.015	Antimony	Sb	nd	Uranium	U	nd
Copper	Cu	0.010	Tellurium	Te	_	Total		**60.8**

Values are weight %   nd = not detected   _ = not measured

22% calcium, and 14% chromium in deposit

CHEMISTRY TIME - Hexavalent Chromium Formation

- Chromium oxide forms as a stable oxide on exposure to air or from corrosion of chromium containing metals
  - **Cr_2O_3 -** Chromium in III oxidation state – trivalent, non toxic
  - Melting point = 2,435 °C / 4,415 °F
  - Boiling point = 4,000 °C / 7,232 °F
  - Once formed – should just remain on metal surfaces
  - Trivalent chromium (III) essential trace mineral in diets – lack of leads to “chromium deficiency”

CHEMISTRY TIME - Hexavalent Chromium Formation

- However – take chromium oxide and add heat, oxygen and a source of calcium following reaction occurs;

- **$2Cr_2O_3$ (Chromium (III) Oxide) + $3O_2$ + 4CaO (Calcium Oxide) = $4CaCrO_4$ (Calcium Chromate (VI))**

- Calcium chromate is a ionic solid, will not enter the gas phase and remains as a solid on the surface of the material (2,710 °C / 4,910 °F melting point). The calcium acts as a “chromate trap” keeping it on metal surfaces

- Calcium oxide is in some anti-seize pastes and also in most insulation/lagging materials

- Calcium fluoride also in some pastes but no reaction occurs – Calcium+fluoride bonds too strong to break

Calcium Oxide Sources

- For GT/ST – if anti-seize paste used that contains calcium oxide then reaction will occur at temperature if oxygen is also present
- For steam lines and HRSG cladding need water to move/leach insulation calcium oxide to high temperature metal surfaces with oxygen present
- HRSG casing – rain water leaks online or during outages followed by corrosion/reactions
- For steam lines – rain water lagging penetration likely during outages followed by corrosion/reactions
- Or humidity during offline periods

Anti-Seize Pastes

- CaO and CaF formulations (with graphite) developed as high temperature, metal free (no nickel) anti-seize pastes – “environmentally friendly”
- Other and older formulations are heavy metal based
- Key aspect is presence of high concentrations of CaO
- Excessive application of pastes likely exacerbates problems (the more CaO available the more $CaCrO_4$ able to be formed)

What about Sodium Chromate?

- Sodium (Na) normally present in insulation as well and will leach

- Sodium chromate could also possibly form from sodium + oxygen + chromium + heat reaction to give sodium chromate (Na_2CrO_4) which is hexavalent (VI) and yellow

- But – melting point 792 °C / 1,468 °F - if it forms likely to either

1. Volatizes and disperses in GT exhaust gas and exits via stack as gas or fine dust particle – chromates not normally detected in preheater tube deposits etc
2. Possibly reacts with any acids present (small amounts of sulphuric acid from S in the fuel) during stop/start operation onto chromium trioxide (CrO_3) which then thermally decomposes at ~197 °C / ~387 °F) to Chromium (III) oxide which is a solid and trivalent (less toxic)

Risk Management

- Hazard management advice from gas turbine and steam turbine OEMs etc technically correct

- Key is to avoid contact (similar to welding) – skin, mouth, eyes, lungs – **standard industrial hygiene actions should apply**
  - Try not to disturb/turn into a dust – can spray with oil (note still exists as hexavalent chromium)
  - P2 dust mask or full face mask or supplied air mask
  - Nitrile gloves (plus barrier cream on skin)
  - Overalls/Disposable overalls
  - Eye protection
  - Clean up before food/drink ingress
  - Any contaminated material should be treated as hazardous waste and disposed of correctly or decontaminated* (see later)

- Deposit removal should be done with care to avoid dusts and skin contact

Risk Elimination

- For GT/ST – if possible do not use calcium oxide containing anti-seize pastes in high temperature and oxygen environments or do not over apply

- For HRSG casings critical aspect is to prevent rain water ingress tha causes corrosion of the SS and that allows calcium oxide leaching onto gas side surfaces with high chromium liner materials
  - Main gas pass/doors
  - Roof spaces
  - Lower crawl spaces

- Or use calcium free insulation in contact with chromium containing liner plates etc in the hot end of the HRSG – no calcium present no calcium chromate formation and retention

- However – need to assume insulation side of stainless steel liner plates (GT exhaust duct) have calcium chromate present on them due to moisture + insulation contact

Bright yellow HRSG gas side deposits on chromium containing metal surfaces should be considered a major warning sign and treated with significant caution

Risk Elimination

- High energy chromium containing pipe work
  - Need to eliminate/minimize rain water ingress offline (control CUI) on at risk materials
  - For bolts etc - do not use calcium oxide containing anti-seize pastes in high temperature and oxygen environments

- Consider non calcium containing insulation for these locations if available

Calcium Chromate Removal/Decontamination

- Addition of a chemical reducing agent will convert Chromate (VI) to trivalent (III) chromium – chromium (III) oxide (Cr_2O_3)

- Siemens current technical advice is to spray deposits of hexavalent chromium with an ascorbic acid ($C_6H_8O_6$ or $HC_6H_7O_6$ aka Vitamin C) or citric acid ($C_6H_8O_7$) solution (~10%) combined with some surfactant (for surface wetting)

- Likely possible reactions (as ascorbic) is as follows

$$\mathbf{12\ CaCrO_4\ (VI) + 9\ C_6H_8C_6 = 12\ CaCO_3 + 6\ Cr_2O_3\ (III) + 10\ C_6H_6C_6^{*} + 6\ H_2O}$$

***ascorbic acid oxidises to dehydroascorbic acid – can be used as a oxygen scavenger**

- Residue (chromium (III) oxide (Cr_2O_3)) can then be rinsed away with demin water. Reaction reported to take 10-15 mins until negative field test result

Calcium Chromate Removal/Decontamination

- Reports from field indicate it works and is an easy and effective solution to chemically converting the at-risk form of chromium (VI) to the less toxic form of chromium (III)

- Could be considered as a HRSG/steam pipe deposit spray which is then cleaned up to prevent any other corrosion of surfaces from residual weak acid solutions

- Could also be used to decontaminate clothing (soak overalls etc in bucket of solution + then rinse with clean water) or equipment but be aware of weak acid solution causing potential corrosion/damage to materials (harness etc)

- Ascorbic acid is a weak acid (pKa = 4.2, carboxylic acid) so similar to vinegar (acetic acid - CH_3COOH) and is easily oxidised

Unconfirmed/Additional Risk Areas

- Review of historical inspection photos have identified other possible, likely calcium chromate HRSG locations

- Upper and lower crawl spaces with;
  - High chromium pipework
  - High chromium liner plates
  - Oxygen atmospheres
  - High temperatures
  - Calcium oxide containing insulation
  - Potential for rain water ingress that allows for calcium leaching

- For HRSGs
  - **SH/Evaporator upper and lower crawl spaces**
  - **GT Exhaust duct work – insulation side of plates mainly**
  - **Gas turbine once through coolers**
  - **No sampling and confirmed laboratory testing to date**

Lower Forward HRSG Crawl Space – Yellow/White Deposits

Upper Forward HRSG Crawl Space – Yellow/White Deposits and Hangers

Image courtesy of HRST

GT Exhaust to HRSG Transition – after rain water ingress

Gas Turbine Once Through Coolers

GT Exhaust Duct Plates – Insulation side of plates

Note ascorbic acid decontamination underway

GT Exhaust Liner Plates Example

- High chromium metal
- Calcium containing insulation
- Yellow color visible at metal/insulation interface – samples collected
- Positive 3M field test result
- Spray decontaminated with ascorbic acid – 15 mins later negative 3M test
- BUT – sample under XRD/XRF analysis did not give a positive result for calcium chromate – below analyser detection levels (needs to be more than 1% to get a hit for XRD)
- Chromium in XRF analysis was only 0.285% so very low levels
- Enough to be visible, give a positive field test result but not enough to be confirmed analytically –lower risk

Summary

- Hexavalent chromium on gas path surfaces that contain chromium (cannot get with carbon steel) is another historical risk associated with power plants – has always been present in plants with welding and chemical cleaning wastes and similar, robust, effective management strategies apply to minimize health and safety risks

- **Hexavalent chromium is a known toxic carcinogen/health risk and associated risks need to be managed carefully at all plants with proven, effective and standard industrial hygiene techniques – no reasons why effective and safe management cannot be carried out with minimal disruption to current work practices**

- Risk management is well understood from welding and industrial handling of chromate materials – key is to avoid contact and this can be safely done during outages etc with sufficient planning, equipment and PPE without a major impact on work flows etc

Summary

- Discontinuation or limiting use of calcium oxide containing anti-seize pastes for GT and ST application will significantly lower risks as without calcium, calcium chromate cannot be formed

- Consider replacement of calcium oxide containing insultation in contact with chromium containing materials

- Field testing of hexavalent chromium can be done with commercial test kits easily – very low detection limit/sensitivity

- **Reaction with 10% ascorbic acid solutions will chemically reduce hexavalent chromium (VI) to the less toxic trivalent chromium (III) and removes the risk. Solutions can also be used for decontaminating equipment etc (note weak acid solution)**

- Minimization/elimination of water leaching of calcium oxide from insulation onto high chromium pipes and HRSG gas path surfaces will lower risks

Hexavalent Chromium Risks for Fossil and CCGT Plants
Sources, Sinks, and Risk Management (plus chemistry)

thermal chemistry

HRSG Forum Virtual Training 2021

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Includes technical information from
Nick Sarkis – ALS - Australia

ALS

NEW ZEALAND Association for the Properties of WATER & STEAM

Tō AOTEAROA Ranga mō ngā Āhuatanga o te WAI ME TE MAMAOA

HRSG FORUM WITH BOB ANDERSON

SINCE Online 2003 COMBINED CYCLE JOURNAL