#### Safety and Design Considerations for CP of Marine Structures

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## **Presentation Aims**

- Provide information for guidance on the design and safety related considerations for marine CP systems.
- Identify some of the main factors that CP designers and facility operators should take into account in relation to Impressed Current Cathodic Protection (ICCP) and sacrificial anode design and operation for marine structures.



## **Presentation Outline**

- Review guidance given in standards in relation to;
- > CP design considerations for petroleum product handling installations
- > ISGOTT requirements for marine facilities
- > Diver safety requirements and CP system design considerations
- > Incendive ignition risk from CP current flow in pipework
- > DC stray current interference risks during construction and CP operation
- > CP T/R unit construction features to provide enhanced safety and operability
- > Gas evolution and safety related considerations on windfarm structures
- > Incendive ignition risk from sacrificial anodes in ballast tank CP systems



#### **Standards for CP of Marine Structures**

- Modern standards for CP of marine structures provide limited guidance on the safety aspects of CP system design and operation.
- BS EN ISO 13174 states "International Standard does not address safety and environmental protection aspects associated with cathodic protection to which national or international regulations apply".
- The older CP standards now withdrawn namely BS 7361 Part 1 and CP 1021 did however provide useful guidance on safety related matters associated with CP system operation.
- Similar guidance on Health, Safety and Environment is stated in NACE standards; "International standard may not necessarily address all potential health and safety problems or environmental hazards associated with the use of materials, equipment, and/or operations detailed or referred to within standards"

### BS 7361 and CP 1021 Guidance

- a) A two-pole isolator should be provided on the CP system DC output to ensure that the DC circuits entering a hazardous area can be isolated.
  - b) When groundbeds are placed in open water, possible dangers to bathers or fish should be considered. The risk is greater in fresh water than in seawater.
  - c) Cathodic protection systems that are to operate where flammable concentrations of gas or vapour may occur should conform to the statutory and other safety regulations.
  - d) Cathodically protected pipework will have a portion of the protection current flowing through it. Any intentional or unintentional disconnection, separation or breaking of the pipework would interrupt the current flow and may produce arcing depending on the magnitude of the current.
  - e) Use of double wound isolating transformers for CP TR units
  - f) Checks to confirm that all piles are bonded into the CP system during commissioning

### **Standards and Changes over Time**

- The older standards had a lot of good guidance and we seem to have forgotten that.
- When standards are updated, we should ensure that guidance where useful and practical is still included

#### WITHOUT A SINGLE DEGREE , THEY BUILT US ROADS THAT HAVE LASTED AN ETERNITY



AND THEN, ENGINEERS ARRIVED



# **Instruction of Personnel**

- In locations where CP related hazards may occur, it is essential that personnel be suitably instructed, and durable warning notices should be authoritatively displayed.
- Suitable written procedures and work authorization permits should be included in the CP system operations manual.
- The guidance given above is extracted from BS 7361 Part
  1 but is not provided in modern CP system standards



#### **CP System Design-Competency**

- BS EN ISO 15257 defines the competency requirements for CP system designers and has improved CP system designs.
- Marine facility operators should note that CP designers, even if BS EN ISO 15257 certified, may not have the requisite levels of electrical and safety design competency for electrical systems in hazardous areas.
- If in doubt, CP system designers and facility operators should seek expert advice.
- The presenter's experience is CP system equipment is often not included in DSEAR records and is sometimes omitted from DSEAR inspections.
- The interval between periodic inspections of hazardous area equipment should not exceed three years without seeking expert advice (BS EN 60079-14)

#### **Aspects of New CP Design**

Select appropriate CP system design standards and industry codes of practice

Ascertain if there are any hazardous areas present.

**Confirm pile bonding arrangements** 

Complete CDM design risk register of CP related risks

Ascertain if there is an internal corrosion risk on tubular piled structures, nature of structure corrosion risks, mitigation methods and corrosion monitoring requirements.

# **Design Features**

#### The following features should be considered;

- Locate T/R units outside hazardous areas where possible
- Construct T/R units to a high standard, with no exposed AC terminals, alarms provided, door interlock isolators fitted, surge protection, viewing windows provided to indicate operational status on meters and appropriate warning signs.
- Limit DC output voltage and AC ripple voltage on DC output for diver safety
- Have bunds on oil cooled T/R units to prevent water contamination by oil if a leak in T/R tank occurred
- Double pole isolators for DC output or even AC isolators
- Suitable circuit protection for DC cables with fuses and MCBs



# **Design Features- cont**

- Use armoured cables for CP current carrying cables, if cables cannot be protected from damage in hazardous areas
- Ensure hazardous area equipment has appropriate certification.
- Locate CP drain point or points in non-hazardous area where possible or use suitable means of connection to structure
- Increase number of drain points to reduce magnitude of current injected I at any one point (spark energy is proportional to I<sup>2</sup>) for inductive circuits.
- T/R units should have phase failure relay to prevent high AC ripple exposing divers to risk
- Use armoured cables for reference electrode circuits and do not route reference electrodes with power cables

### **Relevant Documents**





A Justification into the Use of Insulation Flanges (and Electrically Discontinuous Hoses) at the Ship/Shore and Ship/Ship Interface

#### Contents Effect of Copocitorice Bockground · Research · Multiple Looding Arms and Parallel Circuits · Electrical Characteristics of Cargo Transfer Testing of Insulption Florges · Conclusions and Recommendations Houses Supporting Colculations · References Inductive Circuits Definitions Exemples Showing the Effects of Hose Resistance Appendix 1 and Inductoria · Acknowledgements

7TTO con Lie ach Office: 17 0: Holorfa Piece: Lancon, EC3A 6DG 444.0/1077 85811114 - Lunial: waxwand@pig.to.org - Fac: +++ 5/1207 625 3103 International Chamber of Shipping Oil Companies International Marine Forum - International Association of Ports and Harbors

ISGOTT

International Safety Guide for Oil Tankers and Terminals

REVISED RECOMMENDATIONS ON THE SAFE TRANSPORT OF DANGEROUS CARGOES AND RELATED ACTIVITIES IN PORT AREAS





**IACS** 

### **More Documents**

Guidelines on earthing/grounding/bonding in the oil and gas industry

Model code of safe practice

Part 1

The selection, installation, inspection and maintenance of electrical and non-electrical apparatus in hazardous areas

9th edition



A Practitioner's Handbook for potentially explosive atmospheres

> Publication 186 Edition 7









### **Last Ones**

BRITISH STANDARD

BS EN 60079-14:2003

#### Electrical apparatus for explosive gas atmospheres —

Part 14: Electrical installations in hazardous areas (other than mines)

Protection Against Ignitions Arising Out of Static, Lightning, and Stray Currents

API RECOMMENDED PRACTICE 2003 EIGHTH EDITION, SEPTEMBER 2015

REAFFIRMED, MARCH 2020

The European Standard EN 60079-14:2003 has the status of a British Standard





## ISGOTT

ISGOTT states that "Due to possible differences in electrical potential between the ship and the Jetties, there is a risk of electrical arcing at the manifold during connection and disconnection of the shore hoses or loading arms. This is due to the significant currents that are available from either the Jetty or Vessel ICCP systems. To protect against this risk, there should be a means of electrical isolation at the ship/shore interface. This should be provided by the terminal".

 "To prevent electrical current flow between a ship and a berth during connection or disconnection of the shore hose or loading arm, the terminal operator should ensure that cargo hose strings and metal arms are fitted with an insulating flange. An alternative solution with flexible hose strings is to include, in each string, one length only of non-conducting hose without internal bonding."

# **ISGOTT Requirements**

Торіс	Comment
Vessel to shore bonding	There should not a direct ship to shore bond or there could be a spark risk due to current flow between the two structures. Current flow can be due to vessel or structure CP system operation or simply due to galvanic current flow from connection to dissimilar metals
Insulated flanges installed in loading arms	These should have a resistance of 10K Ohms when new and when in operation 1K Ohm although not stated in ISGOTT but it is in other documents there should be an upper limit on insulation resistance for static discharge. At 0.5V different between vessel and shore facility with I/F at 1 K Ohm current flow will be 0.5mA and will not result in incendive ignition
Insulated flanges inspection	Insulated flanges should be inspected at least annually, and records of checks maintained
Insulated flange testing	Insulated flanges should be tested with low voltage insulation testers e.g. 25V as there has been instances where 500V insulation checks have ignited flammable atmospheres if present in loading arms
Recommended practice	Ensure Vessel and Jetty CP systems at similar potentials lower the voltage difference between two structures high magnitude of current flow to cause incendive ignition
Other guidance documents	HSG 186 The bulk transfer of dangerous liquids and gases between ship and shore , SIGTTO A Justification into the Use of Insulation Flanges (and Electricity Discontinuous Hoses) at the Ship/Shore and Ship/Ship Interface. IMO Safe Transport of Dangerous Cargoes and Related Activities in Port Areas – Revised Recommendations

## **Diver Safety**



## **Relevant Standards and CoP**

- IMCA D045 is an authoritative document
- It provides guidance on safe working voltages for CP systems and body currents for divers.
- Safe body currents based upon guidance in IEC 60479



# **Diver Safety**

- IMCA D 045 states that CP systems are rarely switched off due to the fact that depolarization can occur.
- However, any intention to carry out diving operations on or in the vicinity of such a protected structure needs to consider the possible risk to the divers from the electrical field off the anodes
- Note IMCA D 045 is applicable to seawater but also for brackish and river water systems. In brackish water and fresh water. The electric field strength is greater at anodes as are recommended safe distances between divers and anodes additional considerations are required.



# **Specific Requirements**

#### IMCA D 045 specific requirements

- DC output voltage on CP systems to be limited to nominal value 24V DC (max 30V)
- AC ripple voltage to be limited to less than nominal value 6V rms (max value 7.5V)
- In fresh water or brackish water then minimum diver to anode separation distances should be increased. It is 0.4m if anode 25A in seawater but 3.9m in freshwater.
- Diver body resistance considered to be 750 Ohms up to 50V and above it is 500 Ohms
- Safe DC current is 40mA but safe AC current less than 10mA
- IEC limits for safe current used in the IMCA document have been based upon 50/60Hz but cover 15Hz to 100Hz. AC ripple voltage on CP TR units is 100Hz for single phase but 300 Hz for three phase supplies and thus AC voltage limits lower as body impedance lower at higher frequency. NB Switchmode CP T/R units ripple frequency is much higher but ripple voltage lower
- Currents in IMCA D 045 based upon those that 95% of population can withstand without defibrillation



#### **Diver Safe Body Currents IMCA D045**



Figure 2 – Allowable ac and dc current in the body

#### **Hazardous Voltages Can Exist at Anodes**

- CP TR units need to have DC voltage limited to safe levels
  i.e. 24V
- The AC ripple voltage on the DC output max 7.5 Vrms.
- Need to ensure AC ripple voltage is limited
- Failure of one phase, lack of smoothing on DC output, incorrect phase rotation or T/R equipment failure can lead to high levels of AC ripple



# **Underwater welding**

- IMCA D 045 gives specific requirements in relation to welding. DC welding operations required for anode installation.
  - DC open circuit output voltage should be limited to nominal value 24V DC (max 30V) but this cannot always be achieved in welding operations. DC welding operations were possible output voltage is limited but open circuit voltage can exceed safe limits
  - AC ripple voltage to be limited to less than nominal value 6V rms (max value 7.5V) need to ensure this is limited to 5% on welding generators
  - Insulating gloves required by divers carrying out welding operation
  - Two pole isolator used to be able to isolate DC circuit in event of emergency
  - Risk assessment to be carried out prior to works
  - Weld return close to work area



## **Current Flow in Pipework**



# **Short Circuit of IJ**

Can get short circuit from pig scaffolding, testing with CP equipment and tools shorting flange I/F.

AC or DC voltages each side of I/J can create spark







# **Flange Testers**



- The internal resistance of these devices is only a few ohms
- If there is an AC or DC voltage present across a flange, then there may be a spark risk on testing
- Have seen this on testing a flange with sparks on making contact with probes
- Currents above a few mA can create a spark dependent upon voltage

# **Disconnection of Piping**

- Cathodically protected and in some cases non cathodically protected pipes will have AC/DC current flowing in the pipe wall. If the pipes are mechanically disconnected, the current flow will be disrupted which could cause sparking.
- An alternative path should therefore be provided for the current when disconnecting any pipework by installing an electrical continuity bond across the intended break.
   The continuity bond should be left in place until the pipe is reconnected.
- In addition it is sometimes advisable to temporarily switch off any transformer-rectifiers affecting the section of pipe being worked on at least 24 hours in advance.





# **Cause of Incident**



- It was later determined the rectifier protecting the piping was on and not locked out at the time of the incident. A cathodic protection cable was found attached to the piping being removed.
- Workers did not recognize the cable attached to the pipe as a potential energy source and did not take action to isolate out all sources of energy.
- Bonding cable design was inadequate to provide continuous bond during a pipe jump. Workers did not consider the potential for pipe movement to defeat the magnetic strength of the bonding cable.
- Flammable product in dead leg was not adequately drained to prevent fire potential.

# **CP on Jetties and Platforms**

- CP current will flow in above ground pipework and earth cables with a Jetty/Platform CP energised
- It will also flow in earthing cables and cable armouring
- Extent of current flow will vary and will depend on where CP current is injected, and the magnitude of current provided by the CP system
- Pipe routing on structure and where I/Fs located is an important consideration.
- When CP system is switched off guidance is to allow 24 hours before disconnection of pipework to allow for structure depolarization
- Insulated flange gasket materials should be fire safe following on from Buncefield guidance.

### Extract from BS EN 60079-11

- BS EN 60079-11 gives spark ignition versus voltage curves for resistive, capacitive and inductive circuits
- Different gas groups have different minimum spark energies to cause incendive ignition
- Incendive ignition can occur when cables or pipes carrying CP current are disconnected
- Inductive and resistive circuits the spark hazard is on disconnection of circuits but for capacitive circuits it is with re-connection



#### **Spark Ignition Curves Inductive Circuits**

- Pipe inductance is low in region of nano Henries
- Inductive circuits spark occurs when circuit is broken
- Spark Energy µJoules is proportional to 0.5 I<sup>2</sup> L
  - > Where I = Current (Amps)
  - L= Inductance (Henry)

Figure 5.3 Inductance Circuits-Ignition Curves at 24 volts for all Circuit Metals



### **EI Guidelines Earthing and Bonding**

Gas Group	Product Example	Minimum Spark Energy µJ
IIC	$H_2$ and $CS_2$	< 45
IIB	H and $C_3H_8$	45 to 80
IIA	CH <sub>4</sub>	> 80







## **DC Stray Current**



## **Stray Current Interference**

- One of the risks that can affect the integrity of marine structures is DC stray current interference.
- Stray current interference where it occurs can result in extremely high rates of corrosion under certain conditions.
- 1 Amp current discharge for 1 year will result in a loss of approximately 9 Kg of steel. If the current concentrates in small area then very high rates of corrosion can be experienced up to tens of mm per year.
- Stray current can be provided from
  - a) Vessel or jetty CP systems
  - b) DC operated equipment e.g. cranes or shore to ship DC supplies
  - c) DC welding operations
  - d) Incorrect polarity of CP systems



# **DC Stray Current**

- Corrosion can be caused by stray current flowing onto and off the pipe. Corrosion occurs where the current leaves the pipe.
- In the past telluric currents were not considered to effect the corrosion rate on buried/immersed pipelines but recent work has shown that these too can be implicated in the corrosion of pipelines. Guidance on telluric interference is given in BS EN ISO 21857.



Telluric currents are currents that flow through the earth and are of geomagnetic origin. Pipelines in certain parts of the earth are more susceptible than others and the currents reach a peak around solar maximum. Plot above is for an offshore line and landfall

#### **Stray Current from DC Welding Operations**

- Personnel involved in welding operations often are not aware of stray current risk
- Similarly construction and operation managers not aware of risk
- Can get very high rates of corrosion in a short period of time many mm per year in some instances
- Need to ensure that weld return connection made as close to component being welded as possible
- HSG 118 Safety in arc welding used to give good guidance but was withdrawn in 2007



Single DC welding source on shore. Single ship may be used for multi operator work



Single DC welding source on shore looped cables from ship B to a common connection on ship A may be used for multi operator work



Separate DC welding source. Loading separate adjacent ships may be used for multi operator work

Where a single welding source is used to undertake two welding operations on ships moored alongside each other. The weld current return conductor should connect the work area to the power source as directly as possible. Other arrangements may result in DC interference and premature perforation of the ship hull could occur.



The layouts shown above could result in stray DC current flow through the water (as shown by the arrows), which could result in corrosion at the current discharge locations on the ship hull



Single DC welding source on shore connected to two adjacent ships with the negative connection made to the power source and each ship there is also a possible return current path via the water as indicated by the arrows, where corrosion is possible at the current discharge location.

Sketch: Typical arrangements for ship welding (Do not connect the negative output of DC welding source to different structures or alternative current paths will exist.

### **Stray Current During Construction**

- If welding process not carried out correctly there can be a stray current corrosion risk
- It is important personnel are aware of the risk
- Awareness is one of the main methods of mitigating risk
- Ensure welding return connection is made to structure being welded so that there is no other paradelle current return path
- DC negative output isolated from earth



# **Correct Polarity**

- Need to ensure that electrical personnel are aware of this risk and the consequences of incorrect polarity.
- There does need to be some training in this respect to electrical personnel on DC systems
- There have been a number of instances where incorrect polarity on CP systems has been experienced.



# **Incorrect Polarity**

- It is essential that the output polarity off new T/R units is checked and verified correct
- When working on T/R units get a CP engineer on re-energisation to check output polarity. It is a requirement of some company standards
- Make sure structure to connected negative terminal, anodes to positive output.
- Incorrect polarity does happen and I have known it on offshore wind farms, subsea pipelines and numerous onshore pipelines

#### **Ship to Shore Bonding-Small Boats**





#### FOUR COMPONENTS ARE NEEDED FOR CORROSION ...





### **CP in Hazardous Areas**



# **BS EN 60079-14**

- BS EN 60079-14-2014 Explosive Atmospheres. Electrical Installation, design selection and erection
  - Electrical installations in hazardous areas shall also comply with the appropriate requirements for installations in non-hazardous areas. However the requirements for non-hazardous areas may be insufficient for installations in hazardous areas.
  - Only suitably certified enclosures may be installed in hazardous areas
  - Need to know area classification, gas group
  - Only armoured power cables may be used unless protected from mechanical damage
  - Portable apparatus should be used in hazardous areas only when its use cannot reasonably be avoided. Portable apparatus should have a type of protection appropriate to the zone(s) of use.
  - Equipotential bonding is required for installations in hazardous areas. Thus CP junction boxes and cable armoring needs to be tied to earth

### **BS EN 60079-14**

No CP equipment should be installed in a zone 0 area\*. These would be typically pits or inside vessels.

Cannot really locate I/Fs outside hazardous areas as they create a Zone

CP drain point or current carrying connections outside hazardous areas

No insulation joints or I/Fs in Zone 0

No non-intrinsically safe equipment

2

\*Note: Zone 0 Area is an area in which an explosive gas atmosphere is present continuously or for long periods or frequently.



#### **Non Certified Box in Hazardous area**

Resistor over heated and could have resulted in incendive ignition if auto ignition temp exceeded for gas





If temperature on resistor had exceeded gas auto ignition temperature, then explosion would have occurred and would not have been contained. Have seen jetty CP system enclosures containing resistors/shunts in hazardous areas. JB installed by mistake in hazardous area

# Valve Pit

- This is a Zone 1 area
- Insulated flanges installed each side of valve
- Surge protection devices installed across I/Fs but not certified for hazardous areas. Zone 1 area in pit surge arrestor only Zone 2 certified
- CP drain point connection made in pit



# **Surge Protection Devices**

#### **Only Zone 2 Certified**



#### **Zone 1 Certified**





# Bonding

Avoid inter-pipe bonding arrangements where bonds are connected in a hazardous area

All pipes should be equipotential bonded to avoid touch and spark potential risks

Flanges should be coated to avoid spark risk caused by inadvertent short circuits e.g. tools across flanges guidance in various Codes of Practice





# **TT and TN-S Earthing**

- Earthing systems in hazardous areas are either a TT or TN-S system.
  Terra is Latin for Earth and the TN-S means earth and neutral are separate.
- These system are installed in hazardous areas for safety reasons as when other electrical earthing systems e.g. Protective Multiple Earthing (PME) are employed disconnection of earth cables or earthed structures can result in a spark risk because of neutral current flow in earth cables or pipework.
- CP does comprise the safety provided by TN-S systems as CP will create current flow in earthing systems and there will be a spark risk on disconnection of earth cables or pipes. Personnel need to be aware of this risk.



### **Ballast Tank CP**



#### Anodes Coated with Paint don't Work that well





### **Anodes in Ballast Tanks**



### **Ballast and Storage Tank Design**

- Never use Magnesium anodes for internal CP of marine structures! This is due to hydrogen evolution risk
- Incendive ignition risk with Aluminium Incendive frictional sparking can occur when light metals or their alloys are brought into contact with an oxygen carrier such as rusty steel. The degree of contact required to produce an incendive spark is low and a light glancing blow can be sufficient to ignite flammable atmosphere.



### **Ballast and Storage Tank Design**

- Classification Societies do permit the use of Aluminum alloy anodes in ballast tanks containing flammable product or adjacent to tanks carrying flammable product provided potential energy of anode plus fixings is less than 275 Joules. Some operators do not permit Al anodes only Zinc.
- Anode Height (H) < W/28</p>
- Zinc anodes are permitted



#### **Gas Evolution Marine Structures**



## **Offshore Windfarm Monopile**



#### **Retrofit Installation of Anodes Offshore Monopiles**

- Within a few days after installation of Aluminum alloy anodes in the internal surfaces of some offshore windfarm monopiles where the monopiles had been freely corroding for some time significant changes to water chemistry and gas evolution had taken place. The water within the monopile was not freely flooding.
- Personnel gas alarms were activated on entry
- Water pH had decreased from 8 to 4
- H<sub>2</sub>S evolution had occurred as evident by smell
- Hydrogen evolution had occurred but not at LEL levels
- CO alarms activated most likely thought to be associated with enhanced levels of CO<sub>2</sub>



## Water Chemistry ICCP

If hydroxyl ions produced at cathode from reduction of dissolved oxygen:

Cathodic reaction:

 $\frac{1}{2} \text{ O}_2 + \text{H}_2\text{O} + 2 \text{e}^{\bar{}} \rightarrow 2 \text{OH}$ 

- If protons produced at anode in case of ICCP anode, then anodic reaction is
- Anodic reaction:

 $2H_2O \ \rightarrow 2H^+ + \ ^1{\!\!\!/_2} \ O_2 \ + \ 2e^-$ 

• The nett pH change would **ZERO** 



## **Acid Production**

If aluminium chloride is dissolved in water the solution is acidic. The solution contains hydrated aluminium ions and chloride ions:

 $AICI_3(s) + aq \rightarrow [AI(H_2O)_6]^{3+}(aq) + 3CI^{-}(aq)$ 

The hexaqua complex ion forms and polarises the water molecules that are attached to the aluminium ion through dative covalent bonds. This makes the hydrogen atoms susceptible to attack from solvent water, which acts as a base. The complex ion is deprotonated, causing the solution to be acidic from the formation of hydroxonium ions  $H_3O^+$ :

```
[AI(H_2O)_6]^{3+}(aq) + H_2O(I) \rightarrow [AI(H_2O)_5OH]^{2+}(aq) + H_3O^{+}(aq)
```

Thus, aluminium chloride when mixed with water can result in a gradual reduction in the solution pH. The extent of pH change will be dependent upon the AICl<sub>3</sub> concentration.

The reduction in water pH affects the CP system and can cause changes in water chemistry

# Water Chemistry SACP

If hydroxyl ions produced at cathode from reduction of dissolved oxygen:

**Cathodic reaction:** 

 $^{1}\!\!/_{2}$  O\_2 + H\_2O + 2e  $^{\bar{}} \rightarrow$  2OH  $^{\bar{}}$ 

Protons produced by hydrolysis of the anode corrosion product then anodic reaction is :

Anode reaction:

 $AICI_{3}(s) + aq \rightarrow [AI(H_{2}O)_{6}]^{3+}(aq) + 3CI^{-}(aq)$ 

 $[AI(H_2O)_6]^{3+}(aq) + H_2O(I) \rightarrow [AI(H_2O)_5OH]^{2+}(aq) + H_3O^{+}(aq)$ 

 The nett solution pH change should move in an alkaline direction as cathodic reaction more efficient in creating alkalinity than anodic reaction in creating acidity

# **Chemical Reactions**

- Calcareous deposit formation and Oxygen reduction at cathode
- $\textbf{B} \textbf{HCO}_3^{-} + \textbf{OH}^{-} \rightarrow \textbf{H}_2\textbf{O} + \textbf{+CO}_3^{-2^{-}}$

#### Anode Reactions

$$AI \rightarrow AI^{3+} + 3 e$$

**C**  $[AI(H_2O)_2]^3$ +  $H_2O \rightarrow [AI(H_2O)5OH]^2$ + +  $H_3O^+(aq)$ 



#### Water Chemistry –What Happens

- If the cathodic reaction is oxygen reduction this reaction should be 100% efficient in creating hydroxyl ions OH<sup>-</sup>
- The Al dissolution reaction is far from 100% efficient in creating protons H<sup>+</sup> so why did the solution become acidic ?
- In the case of AI hydrolysis it will take 3 electrons to produce 1 proton
- If anything the seawater within the monopiles should have become alkaline not acidic !



### Water Chemistry –What Happened

- Hydroxyl ions OH<sup>-</sup> were removed from the solution at the cathode by the formation of calcareous deposits and also Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub>
- Thus, some of the hydroxyl ions produced were not available to neutralize the acid formed by the Aluminum ion hydrolysis
- The current flow to the cathode is split between that in the sea water and the mud zone but all the anode current results in anode dissolution into the seawater there is no corresponding anodic reaction in the mud.
- The net result in stagnant water conditions is that the water will become acidic over time as insufficient OH<sup>-</sup> is available to neutralize H<sup>+</sup>



#### **Chemical Reactions Leading to Gas Formation**

- Carbon dioxide CO<sub>2</sub>
- **1)**  $HCO_3^- + H^+ \rightarrow H_2O + CO_2^\uparrow$
- Hydrogen
- **2)** H<sup>+</sup> + 2e $\rightarrow$  H<sub>2</sub> $\uparrow$
- Hydrogen Sulphide

3) FeS + 2H  $^+ \rightarrow H_2S \uparrow$  +Fe $^{2+}$  if water pH below 5 the H $_2S$  will proceed to air phase

#### Chlorine Evolution ICCP Anodes

**4)**  $2Cl^- \rightarrow Cl_2\uparrow + 2e^-$ 

**5)**  $Cl_2$  +  $H_2O \rightarrow HCI$  + HOCI



#### pH vs Concentration of AlCl<sub>3</sub> and ZnCl<sub>2</sub> in Aqueous Solution – Expanded Range

#### pH vs Concentration for AlCl<sub>3</sub> and ZnCl<sub>2</sub> Solutions



#### **Effect of AlCl<sub>3</sub> additions on pH in Seawater and Aqueous Solution**

#### **Larger Concentration Range**

#### **Reduced Concentration Range**





## **Questions**?

