

Slide 1



Corrosives

Slide 2

Aim & Objectives

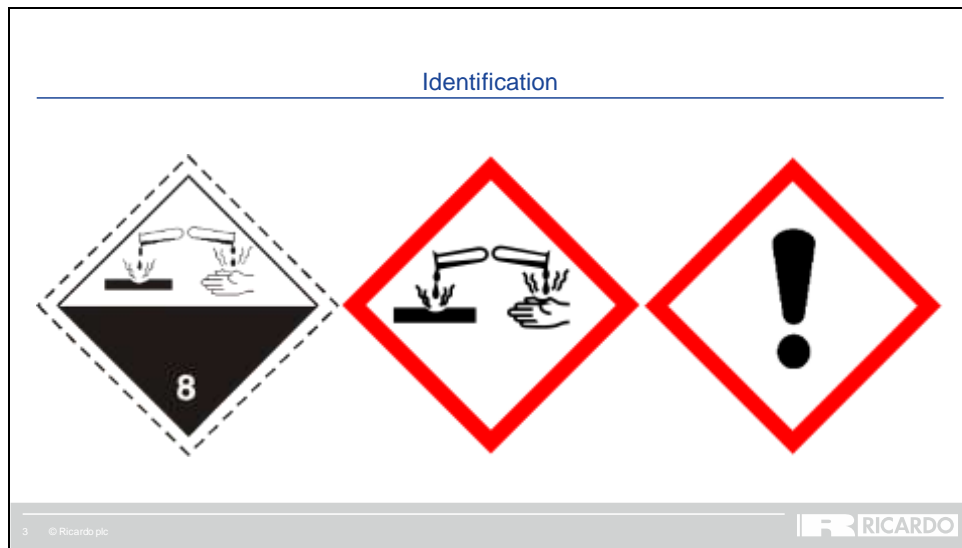
The aim of the session is to introduce the properties, behaviours and types of corrosive substances

Objectives

- Identify corrosive materials
- Describe how corrosivity is commonly measured
- List the general behaviour of corrosives
- Describe the effect different types of corrosives have on the body
- Explore the hierarchy of control for dealing with corrosive substances.

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- Corrosives are identified by the shown imagery; with the transport symbol on the left and the supply (GHS) symbol in the middle.
- Materials that carry the exclamation mark and are labelled as IRRITANT, are corrosives substances that are de-classified as a corrosive, due to concentration.
- The key things to note is that corrosives are not just corrosive to flesh, but also to materials, with extra credence given to the reaction with metals
 - The reaction between corrosives and metals generates further hazards, including (in most cases) the generation of Hydrogen gas, but at the very least, corrosion to metals can occur leading to weakening of containment vessels over time or the damage and potential destruction of equipment and PPE.
- Another key identifier will be their name; in chemical nomenclature (naming systems), corrosives can be determined to be strong or weak depending on their given name, this can be identified with knowledge and practice, but best left to scientific advice
- Corrosives can come in many shapes and forms including solids, liquids and gases
 - With the exception of bases and some organic acids (explained later), almost all corrosives can dissolve in water; this of course can be exploited in the realms of decontamination, minimising hazards, reducing risks from corrosive fumes and gases
 - Being soluble however has a disadvantage when it comes to initial contact with people (most of a human is made up of water) and any release into the environment
- A crucial aspect in assessing risk for corrosives (other than the strength), will be concentration. Concentration fundamentally determines the available amount of corrosive to attack something.
- Two key parts to a corrosive hazard: Strength (corrosive 'power') and Concentration (amount of corrosive available)

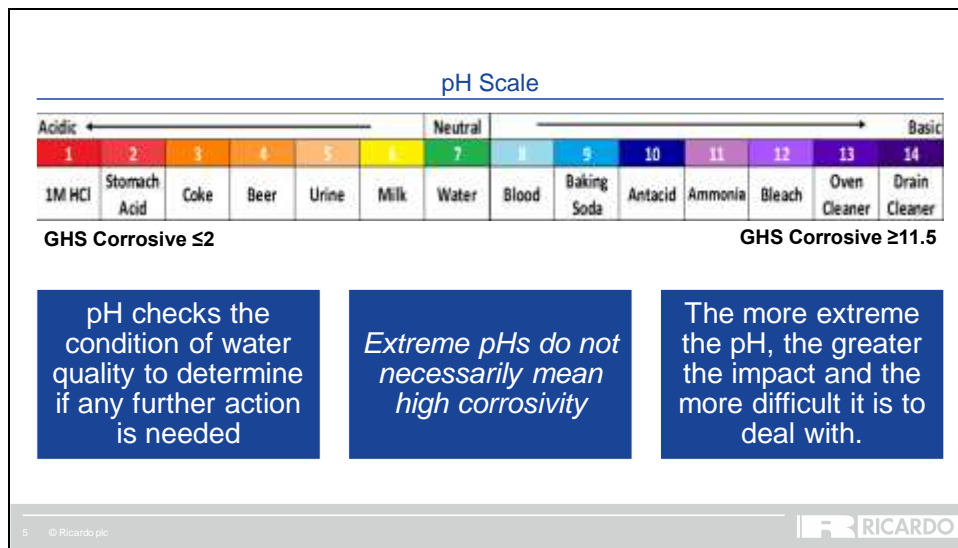
What are corrosives?

Corrosives are chemicals that have the ability to react and attack other substances without initiation or 'trigger'

- Irreversible reaction
- Generate heat
- Degrade / break other chemicals
- Can be slow, can be fast
- Some can react with a select group of metals to produce hydrogen
- React violently with their 'opposite'

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- Corrosives are, in their nature, reactive substances, they require no initiation for them to react with other materials
 - Temperature will increase the rate and onset of any reaction – even in low concentration corrosive solutions, if they are hot, the extent of the reaction will be greater
- The generation of heat is a big deal when corrosives react; they undergo exothermic reactions and often this can lead (very quickly in some cases) to an immense amount of heat being generated. To the point that the majority of a 'corrosive burns' are actually due to thermal burning
- As a chemical reaction is taking place, new products are being formed, these might be innocuous (in the case of neutralisation), or they could be just as bad or be another more prominent hazard (such like the generation of a toxic gas)
 - In combination with the exothermic behaviour, a lot of concentrated corrosives can also decompose or liberate corrosive fumes (due to this heat) adding to the hazards already there (Hydrochloric acid will fume upon heating to release Hydrogen Chloride gas, Nitric acid can decompose to release a mix of Nitrogen oxides (No_x))
- Simply put, speed and extent of a corrosive reaction will depend on three primary factors; strength, concentration and temperature. With all of these factors being proportional to severity as they increase i.e. increase strength, increase concentration, increase temperature = greater severity of corrosive reaction (corrosivity)
- As we will see on the next slide, corrosives are split into two camps, Acids and Bases (with Alkalis being in the camp of bases). These are opposites on the spectrum of corrosives and an acid and base can react violently
 - Weaponising corrosives are commonly referred to 'Corrosive Attacks', with alkalis being worse and far more dangerous than acids



- The pH scale is used to specify how acidic or basic a water-based solution is. Acidic solutions have a lower pH, while basic solutions have a higher pH. At room temperature (25 °C), water is neither acidic nor basic and has a pH of 7.
- The blanket classification of a corrosive under GHS is anything less than or equal to 2 (for acids) and greater than or equal to 11.5 (for Bases and Alkalis)
 - This is because even foodstuffs would need to be transported as dangerous goods and have greater amount of restrictions and costs associated with it. The classification is designed to enable and not disable.
- pH unfortunately does not directly provide information on just how corrosive something is.
 - The more extreme the pH, the harder it is to know just how corrosive
 - Stomach acid is anywhere between pH 1.5-2, which is hydrochloric acid
 - Industrial strength Hydrochloric acid (37%) is a tad lower, around pH 1
 - Stomach acid stays in your stomach and doesn't cause too much damage, but industrial HCl could cause severe and potentially life changing injuries upon contact = pH not a great indicator at the extremes of pH
- We can test for pH using a digital pH meter, or some good old fashioned pH paper.
 - You many have heard of litmus paper, there are two types; blue and red, each targeted towards testing for acids or bases
 - Litmus red targets bases Red = > Blue colour change
 - Litmus blue targets acids Blue => Red colour change
 - Universal Indicator strips (ph paper and solution) targets the entire pH range

FYI BLOOD IS AROUND pH 7.3-7.45 – RATHER THAN 8

Effect of corrosives to the body – addition to thermal burns

Acids	Alkalis / Bases
<ul style="list-style-type: none">• Coagulative Necrosis<ul style="list-style-type: none">–Forms a 'jelly'–This 'jelly' limits body tissue penetration• Attack of the acid struggles to break down proteins and fats (hence the limited effect on the body)	<ul style="list-style-type: none">• Liquefactive necrosis• Denatures proteins and fats... but causes a further process called saponification<ul style="list-style-type: none">– Term used to describe the formation of soap• Saponification does NOT limit tissue penetration

Sensitive areas of the body:

- Eyes
- Mouth / Throat
- Ears

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Acids

- Acids can form a jelly like substance when in contact with flesh
- Acids cannot break-down fats and proteins easily, so this in combination of the jelly formation limits the acids ability to penetrate deep into bodily tissue
- Scab like appearance can form when in contact with skin
- Brown / red discoloration to tissue upon exposure to strong acids
- A milky white appearance (with skin peeling) just like the appearance of skin recovering from severe sun burn can be seen from exposure to weak acids.

Alkalis

- Are great at breaking down fats and proteins in addition to other chemical groups acids can break down.
- This has a severe impact that tissue penetration is not limited and flesh will break-down and 'fall-apart' upon exposure to high concentrations of strong alkalis / bases
- Skin and material surfaces may become very slippery and feel 'soapy' upon base / alkalis spill / exposure
- A crucial aspect to all corrosives; wash affected areas or decontaminate equipment and PPE with water
 - In the case of casualty decontamination = wash for as long as necessary (not just for 15-20 minutes, washing may be required for a long time)
 - Take care not to wash into and across unaffected areas of the body
 - Consider the run-off from washing and do not have personnel or casualties standing in corrosive run-off

Mineral acids



















Acids that do not contain hydrocarbon 'bits'

Often all are strong acids

Most mineral acids are water soluble

Includes: sulfuric, nitric, phosphoric, hydrofluoric and hydrochloric acid.

Mineral inorganic acid

HCl			
H ₂ SO ₄			
H ₂ SO ₃			
HNO ₃			
H ₂ CO ₃			
H ₃ PO ₄			


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- Mineral acids (or inorganic acids) are acids that do not contain any hydrocarbon bits in them.
 - Sulfuric acid – dehydrating and oxidising
 - Nitric acid – oxidising
- Almost all mineral acids dissolve in water
- Mineral acids are considered strong acids and extra precautions should be given, as well as identifying concentrations as a priority.
- Most common mineral acid you will encounter is Sulphuric Acid = Alongside Ammonia, Sulphuric Acid is the most transported chemical commodity in the world.

Organic acids

- Acids that contain hydrocarbon chains
- Acetic acid (ethanoic acid) – vinegar
- Weak acids
- Highly concentrated (glacial) can still cause major damage
- Organic acids can also be flammable (this is from the carbon)



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- Organic acids contain hydrocarbon bits
 - This can add an extra hazard, that organic acids can be flammable
 - Highly concentrated Acetic Acid (common vinegar) is flammable and has a flammable range)
- Organic acids are considered weak acids and not as hazardous as mineral acids
 - Highly concentrated weak acids can cause severe skin burns and must still be considered a major hazard (even though they are “weak”)

Alkalis and Bases – Key Points

All alkalis dissolve in water

- Alkalis are bases that dissolve in water

Alkalis can also be ‘strong’ and ‘weak’

Strong	Weak
<ul style="list-style-type: none"> • Sodium Hydroxide (Lye, or Caustic Soda) • Potassium Hydroxide (Caustic Potash) 	<ul style="list-style-type: none"> • Calcium Hydroxide • Ammonium Hydroxide • Sodium Carbonate / Bicarbonate • Potassium Carbonate • Calcium Carbonate

Bases contain hydro-nitrogen chemical groups (-NH)

Almost all bases struggle to dissolve into water

- A lot of bases also contain hydrocarbon chemical groups

Most are considered weakly corrosive

- Exception to the rule is Ammonia (NH₃)
- It is a strong base that dissolves in water

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Exceptional Corrosives – Hydrofluoric Acid (HF)

- The liquid solution is Hydrofluoric acid, the gas is called Hydrogen Fluoride
- Although not truly a 'strong' acid, hydrofluoric is the most toxic mineral acid
- HF is used & abused to etch glass
- Seeks out and reacts with minerals in the body (Sodium, Potassium, Magnesium, Zinc, Calcium etc)
- It is imperative that exposure to HF is identified:
 - Antidote (sacrificial material) called Calcium Gluconate available to exposures – paramedics now carry it

- Hydrogen Fluoride (gas) or Hydrofluoric acid is a weak acid but incredibly toxic
- Small amounts can cause severed system effects to the body (system effects = symptoms and impact to the body away from the point of contact e.g. HF on skin = effect will be depletion of calcium in blood stream leading to hypocalcemia)
- It is imperative that even 'suspected' exposure is dealt with extreme treatment and prejudice due to the wider impact of the Fluorine on the whole body (not just the corrosive skin burn)
- HF chemically burns nerve endings, little to no pain is associated with HF exposure, delayed pain response can be up to 12 hours after exposure (up to a concentration of 50% HF solution!!)
- Allegedly Wales Ambulance Service doesn't carry calcium gluconate

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Industrial accident in April 2007 whereby a worker was exposed to HF solution through a structural defect in PPE to his thumb

- Always inspect PPE prior to deployment

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Estimated detection of exposure around 6 hrs after due to delayed pain response

- Fluorine is stripping the iron from his blood (and cells) causing the skin to go pale and lose colour



Deterioration of flesh due to the ongoing attack of the Fluorine (not so much the acid components of HF, but the Fluorine is the part that is causing most of the damage here).

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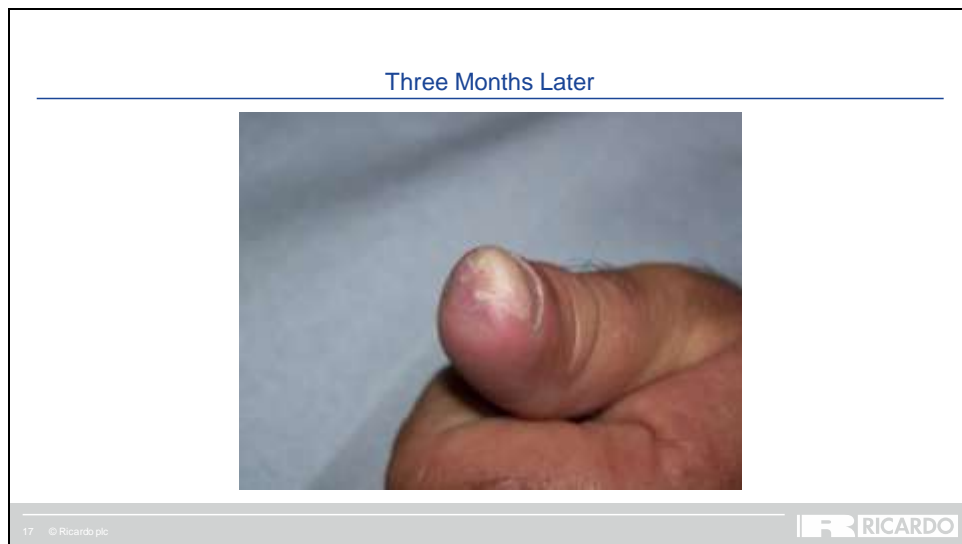
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A very positive recovery considering the injury (I would be considering whether to take the thumb)

- Possible treatment would include; calcium gluconate gel and subsequent dressing, possible local injections of saline and electrolyte solutions (potassium, calcium, iron, etc), dietary supplements to negate the effect of mineral depletion in his body

Corrosives - General Behaviour


Dangerous when wet

Although almost all acids and alkalis (except bases) dissolve in water, they are often sensitive and can react with water exothermically, or endothermically, perhaps even violently

React with opposites


Acids will react with their opposite – alkalis and bases	Can be violent that generates a lot of heat and gas (gas depends on the substances mixing)
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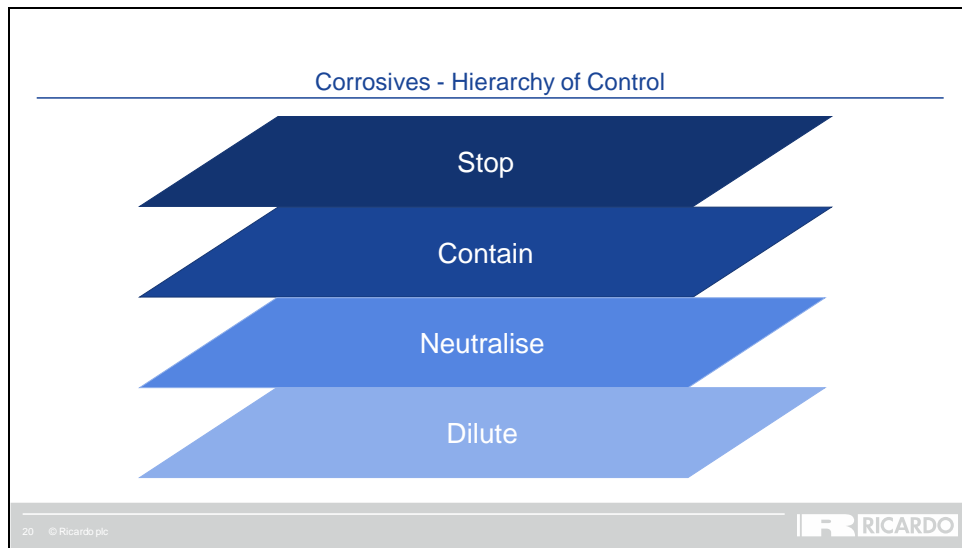
- All of the above depends on the type of corrosive (weak or strong), the quantity and concentration
- Corrosives may decompose under high temperatures and release corrosive fumes.

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- General considerations for corrosives
- Remember that concentrated corrosives can be sensitive water, either generating lots of heat or taking in lots of heat upon contact with water.
- You can overcome this generation of heat by applying more water!
 - This becomes highly advisable during casualty decontamination

Operational Considerations






1. Stop the leak
 - It minimises environmental damage
 - It reduces the operating response time
 - Increases contamination risk – requires greater focus on decontamination and PPE selection
2. Contain
 - Containment is a must to ensure that environmental protection is afforded, and the spread of spill is minimised
3. Neutralisation
 - Usually limited to small scale spills and contamination
 - Neutralisation requires careful monitoring of pH to ensure that the neutralising agent doesn't overshoot the pH generating the opposite hazard (acid into alkali etc.)
4. Dilution
 - Usually only applicable to decontamination and casualty handling measures to very quickly negate the effects of corrosive exposure
 - In contact with waste-water utilities, they may ask for dilution if they have agreed to take a product into the foul sewer and process it at a waste treatment works

CONTAIN

Leak Control Tactics	Containment options:
<ul style="list-style-type: none">• Check position of upstream valves• Check integrity of container openings tighten caps, bungs, lids, etc• Stand-up leaking container• Move container so hole is above liquid/solid level	<ul style="list-style-type: none">• Absorbing• Remote isolation or valving down• Site drainage/ventilation shutdown• Retention, for example drain blocking• Covering, for example, use salvage sheets or foam• Damming• Overpacking• Patching• Plugging• Pressure isolation• Solidification• Vacuuming• Water bottoming• Decanting

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- Leak control tactics are plentiful – employ common sense
- Consider whether contamination will occur due to control tactic
 - This isn't necessarily a problem, but be **PROPORTIONAL**, do not accept high levels of risk for low gain,
 - Planned contamination must be accounted for and dealt with accordingly with suitable control measures in place such as emergency triggers or arrangements in case exposure occurs to responders
- Any absorbent material used takes on the hazard of the substance it is absorbing (socks and pads on liquid flams = those socks and pads are now considered class 3 flammable articles, same goes for corrosives)
 - This means any disposal should be disposed in the same fashion for hazardous waste (whatever the hazard of the absorbed substance is)
 - Finalise exit strategy and identify clean-up measures
- Often, containment is the final step to stabilise the scene and consideration as to ownership responsibilities and any further public safety should dictate what happens next
 - It is advised not to neutralize or dilute large spills and it is not advisable to use these tactics to deal with a spill or leak, they are really only used during decontamination
 - Dilution however can be used to reduce risks water treatment works (upon communication with them of course), if product has entered foul drainage and the waste-water undertaker has agreed to take the product, dilution down the drains may be required.

NEUTRALISE

The use of an acid or base to produce a less hazardous material


- Full neutralisation produces non-hazardous products to people and to the environment

Usually limited to small scale spills

Neutralisation requires careful monitoring of pH to ensure that the neutralising agent doesn't overshoot the pH generating the opposite hazard (acid into alkali etc.)

Conditions:

- Corrosive material must be positively identified = corrosive type, quantity and concentration as a minimum
- Containment and control of spill has already been achieved (for a controlled neutralisation process)
- Sufficient neutralising agent on hand = this can be substantial and on the tonnage scale for large spills
- Sufficient mixing to ensure neutralising agent comes into contact with all the corrosive
- The neutralising agent must not adversely affect the environment
- Mild (and weak) alkalis (e.g. sodium bicarbonate) to neutralise acids
- Mild (and weak) acids (e.g. acetic acid) to neutralise alkalis / bases


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All slide points are crucial to understanding neutralisation as a control tactic

- Critical point is that consideration of scientific advice is sought for this tactic, as estimated amounts of neutralising agent needs to be calculated; therefore quantity, concentration and corrosive type must be identified to ensure this is as accurate as possible
- Neutralisation is very useful however on the small scale for equipment and/or PPE
 - As Neutralisation requires the addition of material, dilution is the favoured option on small scale control.
- Neutralisation can generate lots of heat due to the reaction (unless the 'mixing-pot' has some water or has been diluted first)
 - Neutralisation is not advised as a decontamination tactic

DILUTE

- Requires huge amounts of water
- Used with water soluble solutions
- Must meet following criteria:
 - Is not water reactive
 - Will not generate toxic gas upon contact with water
 - Will not form a solid or precipitate
 - Is totally water soluble
- It is a considered as a last option

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- Dilution is often the last resort when it comes to controlling and dealing with a corrosive material
- Identification of corrosive type, quantity and concentration are all required to assess how much dilution will be required
- Dilution is very effective at reducing concentration, meaning that the risk associated with skin and eye exposure to can be very quickly mitigated
 - The tricky part, is that even dilute corrosives may still be damaging to the environment or via other exposure route (ingestion or inhalation etc.)
- Dilution is the only option for decontamination, consider water sensitivity or reactivity, overcome this by the application of more water.

Decontamination?

Emergency = Use water and dilute by thousands or orders of magnitude

Responders	Equipment
<ul style="list-style-type: none">• Don't get contaminated• Employ 'RRR' controls• Assess levels of contamination• Lightly wash or brush affect areas of PPE (boots and gloves) prior to safe-undress – MINIMISE WATER USE• Consider further washing (after undress) prior to bagging either for disposal or laundry• Contain washings – AVOID STANDING IN WASHINGS	<ul style="list-style-type: none">• Don't get contaminated• Assess levels of contamination• Segregate all equipment for washing (consider washing prior to any disposal)• Wash using minimal quantities of water• Contain washings

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- Emergency =
 - Consider where the washings are going, avoid having casualty lying in the washings = raise casualty up and out of washings
 - Careful use of water (no power washing), wash the casualty and not responders
 - If casualty has been exposed and contaminated on the face, consider possible ingestion of product and subsequent advice for treatment = give small amounts of water for casualty to drink, advise ambulance on possible exposure via ingestion
 - Generally, corrosives can be diluted very quickly due to low quantities associated with contaminated casualties, most of the washing will be 'drawing-out' contaminant from affect skin or eyes to mitigate impact