

Incident Title		Sulphuric Acid Release From Acid Sampling System			
Incident Type		Acid Release			
Date		12 th February 2014			
Country		USA			
Location		Martinez, CA			
Fatalities		Injuries		Cost	
0		2		Unknown	
Incident Description		<p>The sulphuric acid (H₂SO₄) alkylation process produces a high value gasoline blend component (“alkylate”) by reacting light olefins (C₃ – C₅) with iso-butane (iC₄) in the presence of liquid H₂SO₄ acid catalyst to form highly-branched (C₇ – C₉) iso-paraffins. The hydrocarbon/acid mixture leaves the reactors as an emulsion and passes to an acid settler where the hydrocarbon and acid phases separate. The H₂SO₄ acid concentration (strength) in the system is maintained in the range 98.5 - 90.0 wt% to avoid undesirable polymerisation and cracking reactions. Frequent sampling and testing of the acid strength is required to help ensure it remains within these limits.</p> <p>On the day of the incident, 2 operators were reinstating the original acid settler acid sample station (fabricated from tubing) after it had undergone non-routine maintenance. Shortly after the valve which isolated the acid sample station from the acid settler was opened fully, the tubing immediately downstream of the valve separated at a ferrule-type (compression) fitting, spraying the 2 operators with acid. The operators immediately evacuated to a nearby safety shower. Emergency responders transported the 2 operators to a specialist hospital burns unit by helicopter and ambulance (they were only declared fit to return to work after 153 and 173 days, respectively). Acid continued to spray out of the failed joint for more than 2 hours. By the time emergency responders were able to isolate the leak, some 38 tonnes (84,000 lbs) of acid had been released. The state regulator forced the unit to remain shut down until 28-Feb-14 pending completion of a series of abatement orders.</p>			
 <p>Credit: US Chemical Safety Board</p>					
Incident Analysis		<p>Basic cause was failure of a DN 19 (¾" NS) ferrule-type tube joint in the acid sampling system due to inadequate tightening/compression of the joint.</p> <p>Critical factors included: 1) New, inherently safer, closed loop acid sampling systems fabricated from more robust piping were installed in 2010 but were unreliable and taken out of service (this led to the original, less safe sampling systems being reinstated), 2) The tubing on the reinstated sampling system was not leak tested before it was returned to service, 3) The two operators were not wearing appropriate personnel protective equipment (PPE).</p> <p>Root causes included: 1) Inadequate design (acid sampling system), 2) Failure to implement hierarchy of controls (abandoned attempts to make new, inherently safer sampler operable; reinstated old, less-safe sampler relying on administrative controls [sampling procedure and PPE]), 3) Inadequate maintenance procedure (no requirement to leak test process tubing/fittings after modification/repair), 4) Inadequate training (joint integrity), 5) Inadequate PPE (acid suit not provided, face shield incompatible with hard hat + goggles, respiratory protection not specified), 6) Inadequate leadership (production prioritised over safety), 7) Weak process safety culture (operators routinely exposed to hazardous vapour cloud while sampling, failure to learn from multiple acid burn incidents on same unit, failure to enforce PPE standards).</p>			
Lessons Learned		1) A strong process safety culture is necessary to help prevent process safety incidents and avoid injuries to workers, 2) Implement “inherently safer design” principles and “hierarchy of controls” (inherently safe > passive protection > active protection > administrative controls) to mitigate hazards.			
More Information		1) “Tesoro Martinez Refinery Process Safety Culture Case Study”, US Chemical Safety and Hazard Investigation Board, Report No. 2014-02-I-CA (2014): https://www.csb.gov/tesoro-martinez-sulfuric-acid-spill/ .			
Industry Sector		Process Type		Incident Type	
Oil & Gas		Alkylation (H ₂ SO ₄)		Acid Release	
Equipment Category		Equipment Class		Equipment Type	
Mechanical		Piping		Small Bore Connections	