PRAXAIR
Making our planet more productive

Water & Wastewater Treatment

Case Study

Cost and maintenance reduction with CO_2 to replace sulfuric acid for pH control at Steel Dynamics, Inc. (Butler, IN)

Case Study: Cost and maintenance reduction with CO_2 to replace sulfuric acid for pH control at Steel Dynamics, Inc. (Butler, IN)

Overview

The Iron Dynamics Division of Steel Dynamics Inc (SDI) reduced the operating cost of pH control, as well as the maintenance cost related to scale formation, in their cooling water loop, through the replacement of sulfuric acid with carbon dioxide.

The Challenge

The Iron Dynamics facility of SDI has an 800 gpm cooling water loop that makes direct contact with flue gas from a submerged electric arc furnace for emissions control. The loop consists of a scrubber for contact with the flue gas, a thickener and clarifier to remove solids from the scrubber effluent, and a cooling tower. Due to fluctuations in the ore feedstock, large changes in pH are observed in the cooling water, sufficient to raise the effluent water pH above the limit of 9.

Sulfuric acid was added to reduce pH, but cost was high and promoted the formation of gypsum ($CaSO_4$) scale, in conjunction with concentration of the salts due to evaporation in the cooling tower. Gypsum forms at pH levels above 2 and is only slightly soluble (2-2.5 g/L at 25°C). Gypsum scaling at SDI was so difficult to remove that transfer lines had to be replaced. An additional drawback of sulfuric acid is that slight excesses of acid addition can lead to very low pH values (<4), creating acidic process water.

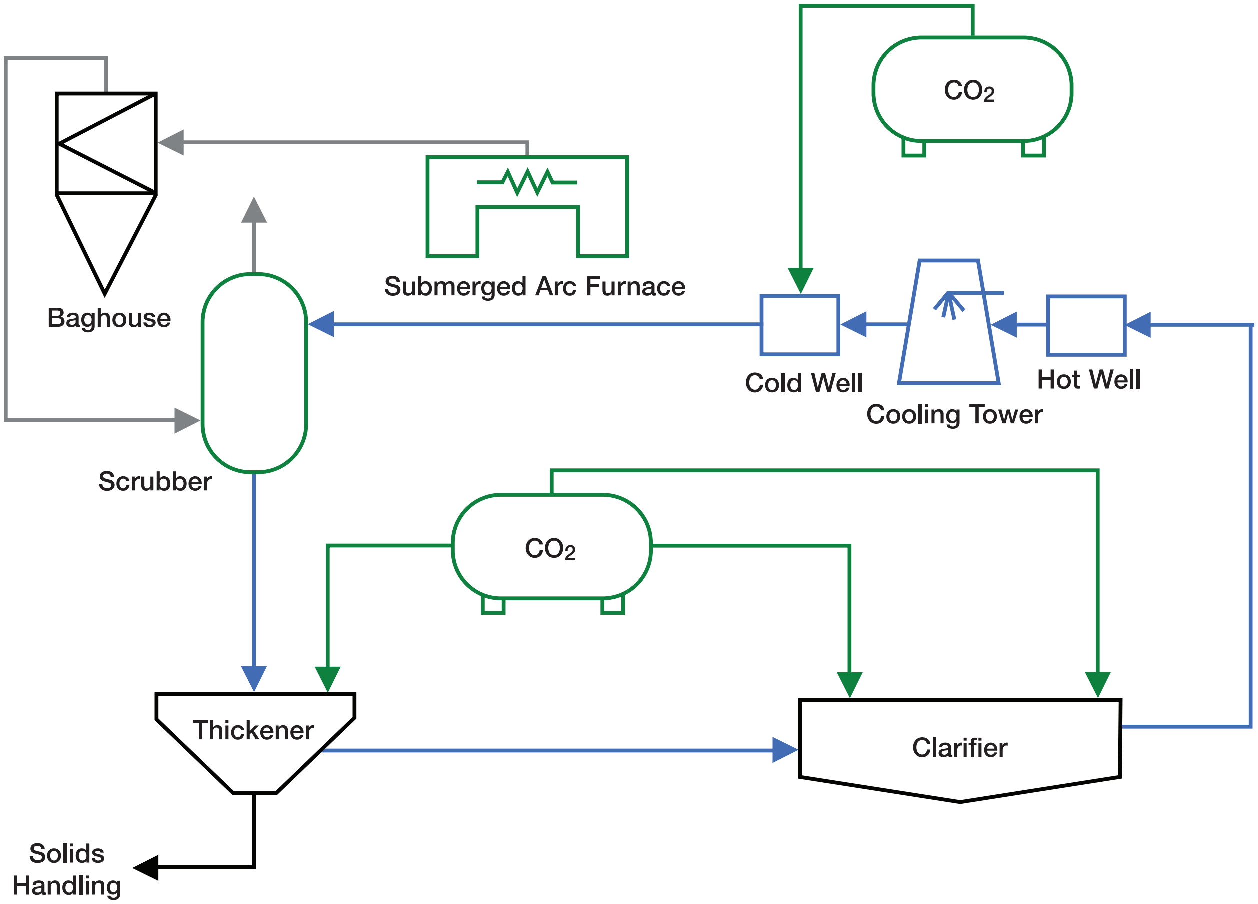
Due to a lower cost and reduced tendency to form scale, carbon dioxide (CO_2) addition to the process water was proposed as a replacement for sulfuric acid for pH control. While carbonate scale is even less soluble (0.013 g/L) than gypsum (2-2.5 g/L), carbonate scale formation can be avoided with pH controlled to below 10. Below pH 10, calcium is in the form of calcium bicarbonate ($Ca(HCO_3)_2$), which is highly soluble at over 160 g/L (25°C). As an additional advantage, excess CO_2 addition leads to a pH value that is close to neutral (6-7) at atmospheric pressure, so there is no risk of overshooting.

Praxair's Proposal

SDI chose Praxair's CO_2-based pH control system. The system features both liquid and gas injection. Four injection points were chosen throughout the cooling water loop: the cold well, thickener, clarifier inlet and clarifier outlet. The various locations required different pH levels. For example, a higher pH (above 11) is maintained in the thickener and clarifier to promote the precipitation of calcium carbonate, which is removed in these unit processes.

Fig.1: The Praxair CO_2 installation at Steel Dynamics, Inc.

Fig 2: The cooling water loop



A small backup supply of sulfuric acid was retained to allow the system respond to sudden swings in ore quality and cooling water composition.

Background

In process waters, divalent ions from carbonic (CO_3^{-2}) and sulfuric acid (SO_4^{-2}) combine with calcium ions (Ca^{+2}) to produce scale. Sulfate (gypsum) and carbonate (limestone) scale differ in the solubility and pH conditions under which they form. As carbonate scale forms only at pH>10, it is controlled through pH reduction and control. However, because sulfate scale can form at most typical operating conditions (pH>2), it requires the addition of chemicals specifically targeted for sulfate scale inhibition.

Scale formation reaction	pH condition for formation	Solubility at 25°C (g/L)	Control Method
$SO_4^{-2}+Ca^{+2}\leftrightarrow CaSO_{4(s)}$	>2	2	Addition of scale inhibitors
$CO_3^{-2}+Ca^{+2}\leftrightarrow CaCO_{3(s)}$	>10	0.013	pH control

Results

As shown in the table, use of CO_2 reduced pH control costs by 35%. Additional savings have been realized due to reduced maintenance, downtime and solids handling (from dredged scale) associated with sulfate scale formation.

Comparison of Annual Operating Cost

	H_2SO_4 Only	CO_2 with H_2SO_4 backup
CO_2 Cost	--	227 TPM @ $79.70/ton = $217k/yr
H_2SO_4 Cost	217 TPM @ $180/ton = $469k/yr	34 TPM @ $180/ton = $73k/yr
Combined Cost	$469,000	$290,000

Plant Highlights

Project Location: Butler, IN

Client: Steel Dynamics, Inc.

Flow: 750-850 GPM

CHALLENGE: Reduce costs of acid usage, mitigate risk of overshooting pH and gypsum scaling.

SOLUTION: Replace acid injection with liquid and gaseous CO_2 in the contact cooling water loop.

ACHIEVEMENTS: less clogging of transfer lines, reduction of recalcitrant calcium sulfate scale, 35% reduction in cost of pH control chemicals, reduced chemicals handling, less downtime for cleaning/dredging, lower maintenance costs.

Reference

[1] V. Hart, T. Crowley, S. Samandi, “Expensive Problem, Inexpensive Solution: Boost Alkalinity With Carbon Dioxide and Lime,” Opflow, September 2009, p. 22-25.

Making our planet more productive™

Printed in the United States of America
6/2015

P-40-4099

Praxair, Inc.
39 Old Ridgebury Road
Danbury, CT 06810-5113
USA

www.praxair.com
info@praxair.com

Telephone:
1-800-PRAXAIR (1-800-772-9247)
(716) 879-4077

Fax:
1-800-772-9985
(716) 879-2040