“Amines 101” for Metalworking Fluids

Houston Section STLE

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Dow Consumer & Industrial Solutions

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Technical Services & Development

Overview

- Application areas
- Neutralizers vs. pH adjusters vs. pH buffers
- Typical acids (good & bad)
- Neutralizer characteristics & choices
- pH adjuster characteristics & choices
- pH buffer characteristics & choices
- Secondary benefits
- Health, safety & regulatory factors

Primary Application Areas

- Water-dilutable metalworking fluids
  - Metal removal (drilling, tapping, grinding, etc.)
  - Metal forming (drawing, rolling, stamping, etc.)

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Neutralizers vs. pH Adjusters vs. pH Buffers

- Neutralizers
  - Typically used in initial formulation (concentrate) to form salts of acid-functional components (organic & inorganic acids)

- pH Adjusters
  - Commonly added to virgin fluids to form stable concentrate/dilution & adjust alkaline pH
  - Sometimes added "tank-side" in MWF systems to restore starting pH of fluid

Neutralizers vs. pH Adjusters vs. pH Buffers

- pH Buffers
  - Added to concentrates to neutralize “bad acids” formed during use of fluid and to prevent pH drop (i.e. provide reserve alkalinity)
  - Sometimes added tank-side to renew buffering capacity of fluid

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Typical Acids

- Functional acids (good)
  - Organic acids such as oleic, tall oil, nonanoic, decanedioic and many others provide: corrosion control, emulsification, lubrication
  - Inorganics such as boric acid & phosphate esters impart: corrosion control, biostatic effects, lubrication

- Acid contaminants (bad)
  - By-products of microbial growth (short-chain organic acids)
  - Carbonic acid from dissolved carbon dioxide
  - Oxidative degradation products (mostly organic acids)
  - External contaminants (acid-based cleaners, etc.)

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The Ideal Neutralizer

- Low Molecular Wt.
  - Less is needed to neutralize a given amount of acid

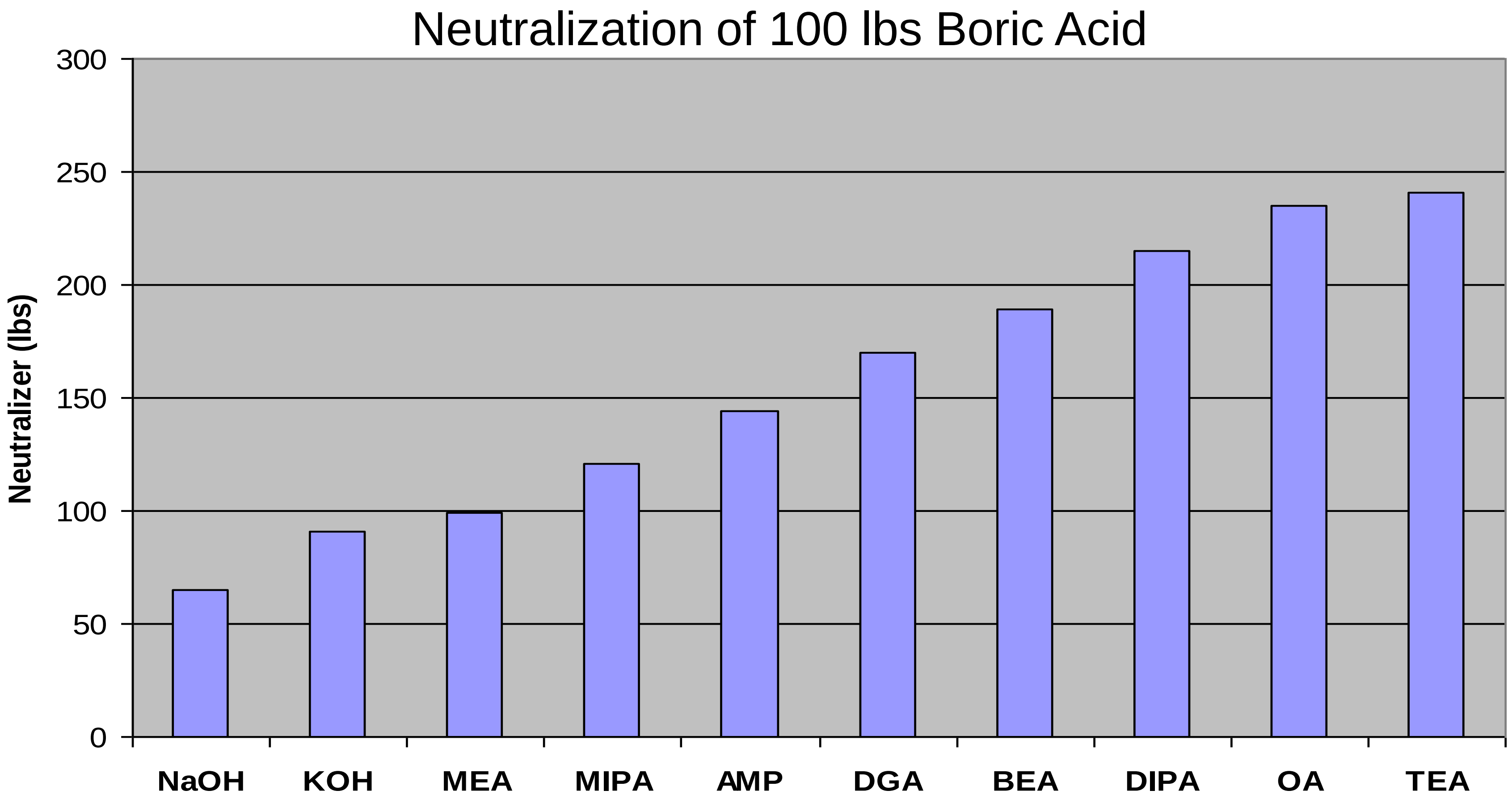
- High Base Strength (pKa)
  - pKa is the pH where ½ the base is neutralized
    - At higher pHs less is neutralized, at lower pHs more is
  - Reaction of highest pKa neutralizer dominates

- Favorable Salt Characteristics
  - A "salt" is the neutralization product of an acid & base (ionic bond)
  - Neutralizers can influence the performance of the corresponding salts
    - Corrosion control
    - Emulsification
    - Solubility
    - Microbial resistance
    - Lubrication

Typical Neutralizers

Neutralizer	Molecular Wt.	pKa	Other Relevant Characteristics
Sodium Hydroxide	**40**	13.8	**Most efficient overall**, lower performing salts (vs. amines), handling hazards
Potassium Hydroxide	**56**	13.5	Lower performing salts (vs. amines), handling hazards
Monoethanolamine (MEA)	**61**	9.5	**Most efficient amine**, microbially degradable (forms ammonia), leaches cobalt, aggressive on Al alloys
Monoisopropanolamine (MIPA)	**75**	9.6	Slightly better microbial resistance (doesn't release ammonia), leaches cobalt
Aminomethylpropanol (AMP)	**89**	9.7	Good microbial resistance (doesn't release ammonia), leaches less cobalt
Diglycolamine (DGA)	**105**	10.0	Microbially degraded (fungi), leaches less cobalt
Butylethanolamine (BEA)	**117**	10.0	Enhances biocide performance, secondary amine
Diisopropanolamine (DIPA)	**133**	9.0	Some microbial resistance, secondary amine
Octanolamine (OA)	**145**	9.8	Significantly enhances biocide performance, maintains good ferrous corrosion control
Triethanolamine (TEA)	**149**	7.8	**Least efficient**; microbially degradable (forms ammonia), leaches cobalt

Neutralizer: Molecular Wt. Impact



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The Ideal pH Adjuster

- High pKa
  - High base strength equals efficient pH development

- Minimally reactive with atmospheric CO_2

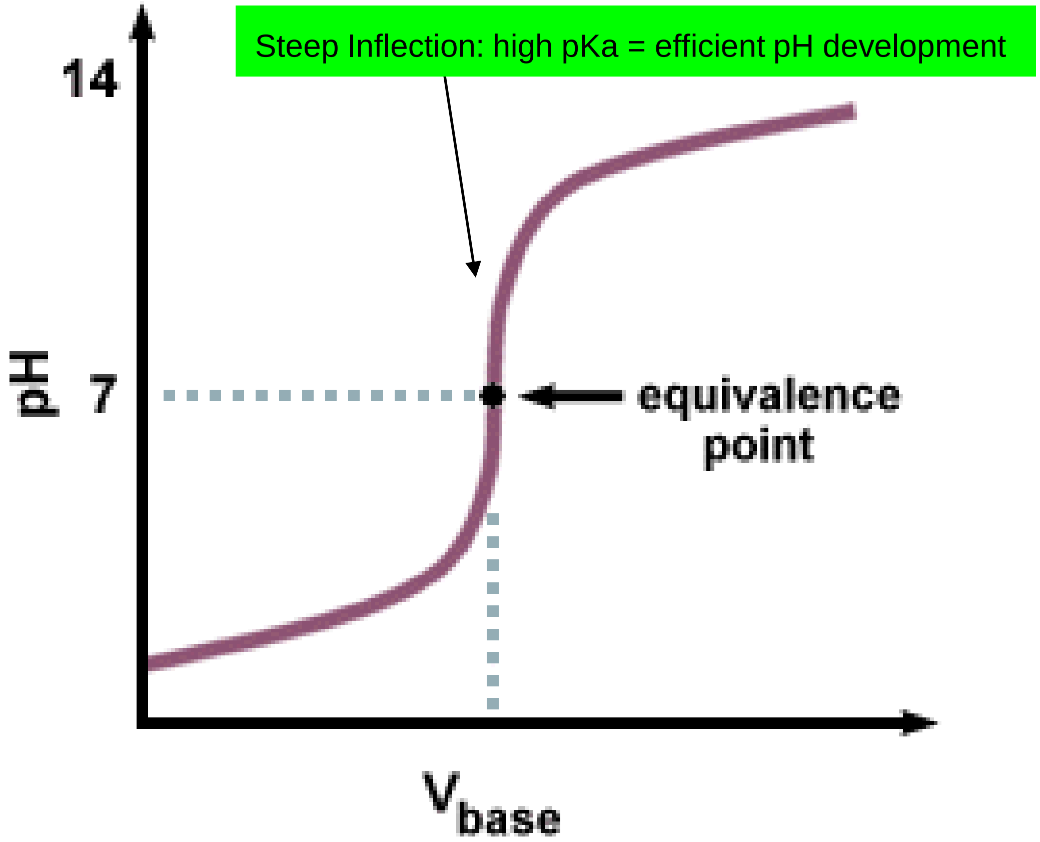
Typical pH Adjusters

pH Adjuster	pKa	Molecular Wt.	Other Relevant Characteristics
NaOH	**13.8**	40	**Most efficient overall**, highly reactive with atmospheric CO_2
KOH	**13.5**	56	Highly reactive with CO_2
DGA	**10.0**	105	**Most efficient amine (tied)**, moderately reactive with CO_2
BEA	**10.0**	117	**Most efficient amine (tied)**, not tested for CO_2 reactivity
OA	**9.8**	145	Not tested for CO_2 reactivity
AMP	**9.7**	89	Less reactivity with CO_2
MIPA	**9.6**	75	Moderately reactive with CO_2
MEA	**9.5**	61	Moderately reactive with CO_2
DIPA	**9.0**	133	Not tested for CO_2 reactivity
TEA	**7.8**	149	**Least efficient**, not tested for CO_2 reactivity

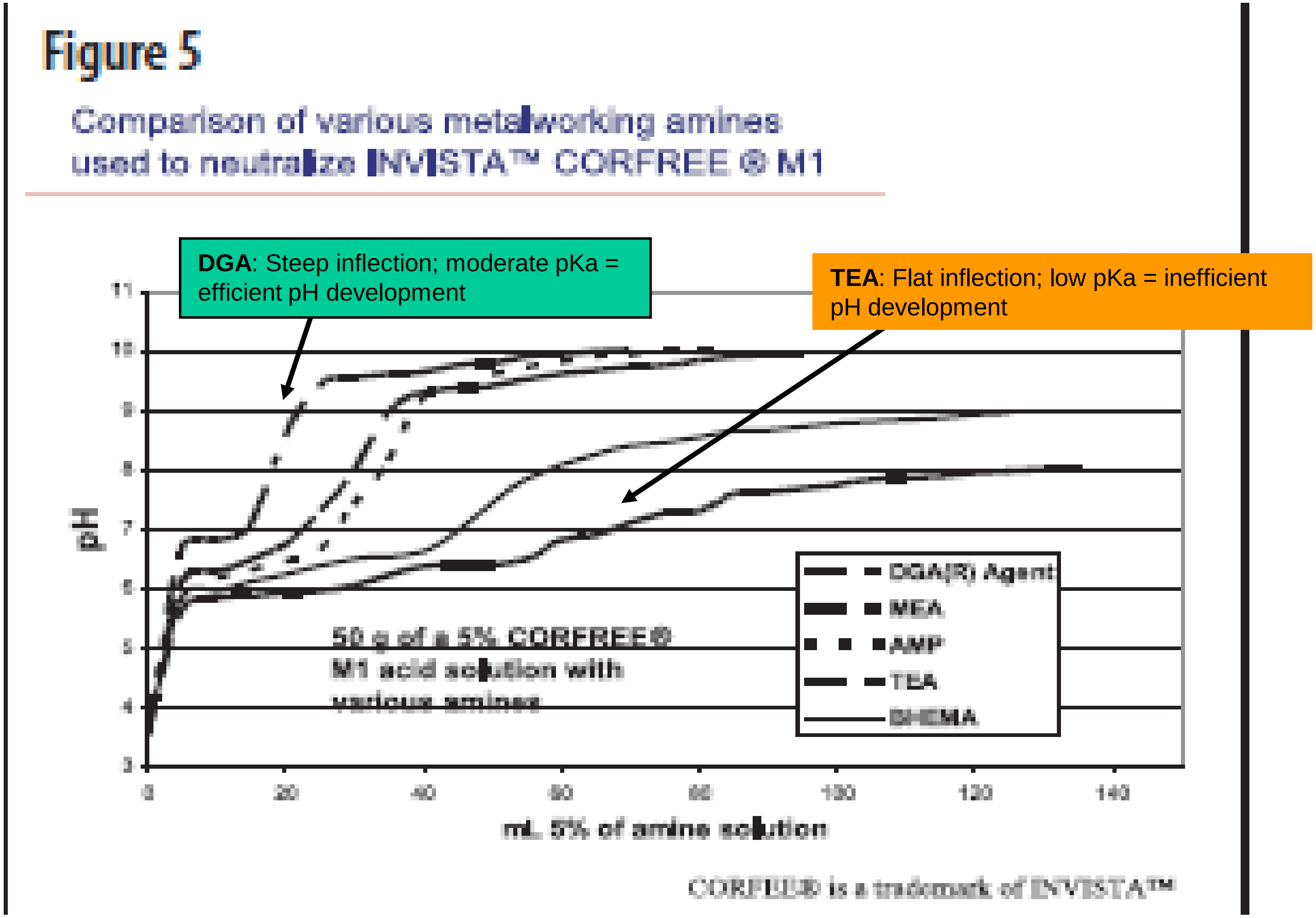
pH Adjuster: Base Strength Impact

- KOH & NaOH
  - Strong bases
- Amines
  - Moderate to weak bases

NaOH or KOH Titration Curve



Amine Titration Curves



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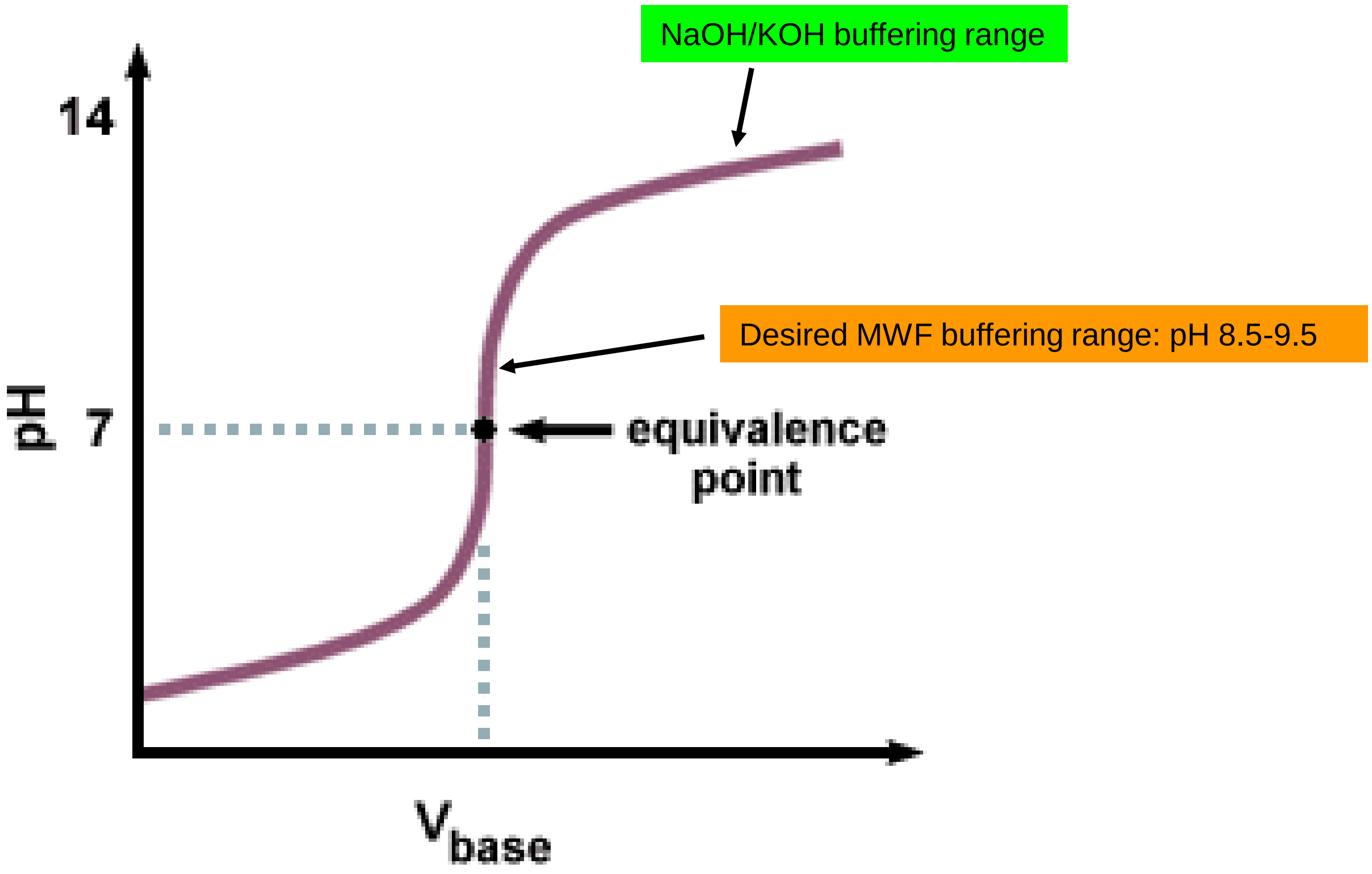
The Ideal pH Buffer

- Flat pH response in desired pH range
  - Flat titration curve
- Low molecular weight
- Low reactivity with CO_2
- Good microbial resistance

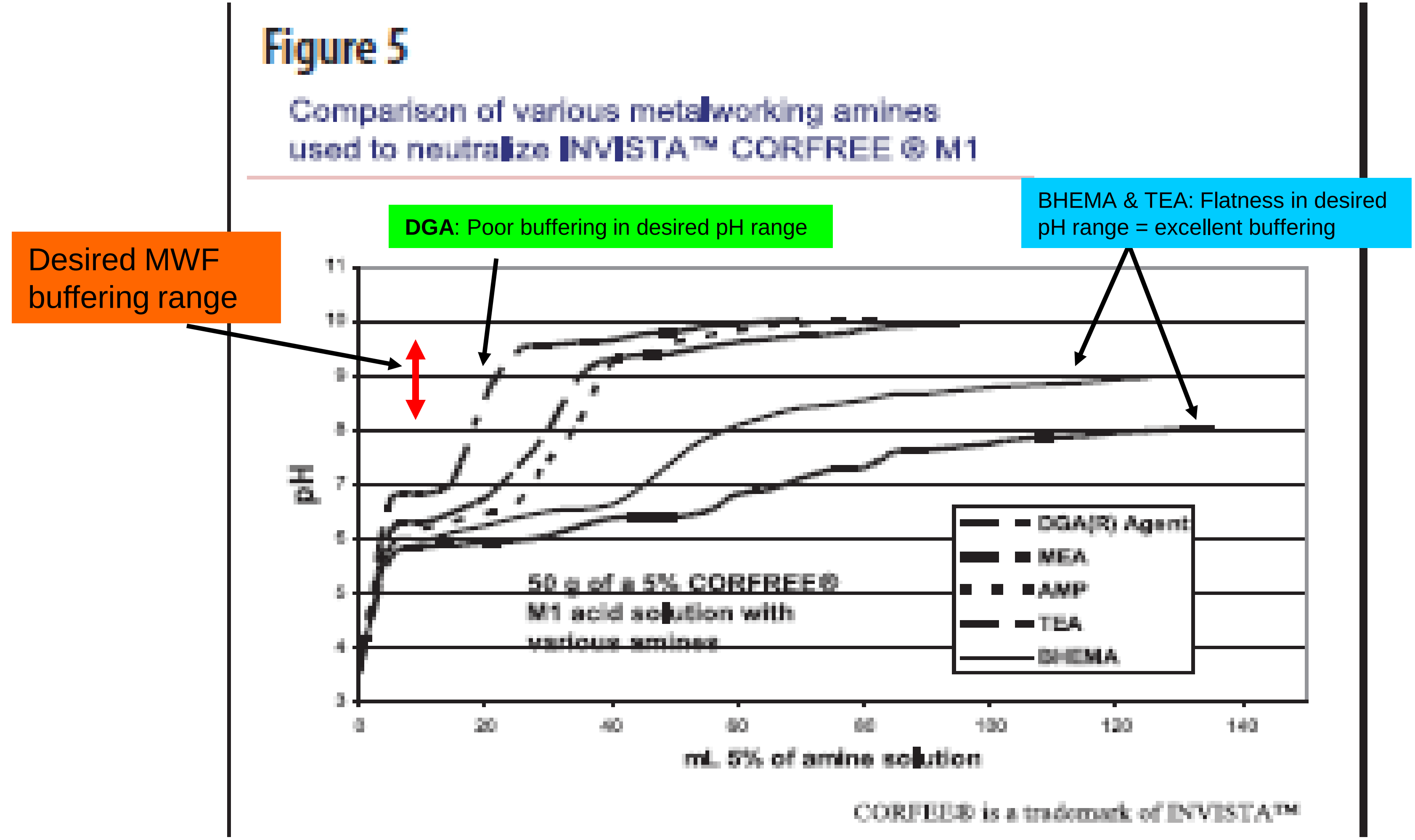
Typical pH Buffers

pH Buffer	Low pKa = flatness in MWF pH range 8.5-9.5	Molecular Wt.	Other Relevant Characteristics
TEA	**7.8**	149	**Flatest titration curve = best buffer**, highest molecular wt., highly degraded by microorganisms
DIPA	**9.0**	133	Some microbial resistance, not tested for CO_2 reactivity
MEA	**9.5**	61	Readily degraded by microorganisms, reactive with CO_2
MIPA	**9.6**	75	Some microbial resistance, reactive with CO_2
AMP	**9.7**	89	Good microbial resistance, less reactive with CO_2
OA	**9.8**	145	Excellent enhancement of biocide performance, not tested for CO_2 reactivity
DGA	**10.0**	105	Microbially degraded (fungi), reactive with CO_2
BEA	**10.0**	117	Very good microbial resistance, not tested for CO_2 reactivity
KOH	**13.5**	56	**Steepest titration curve = worst buffer**, highly reactive with CO_2
NaOH	**13.8**	40	**Steepest titration curve = worst buffer**, highly reactive with CO_2

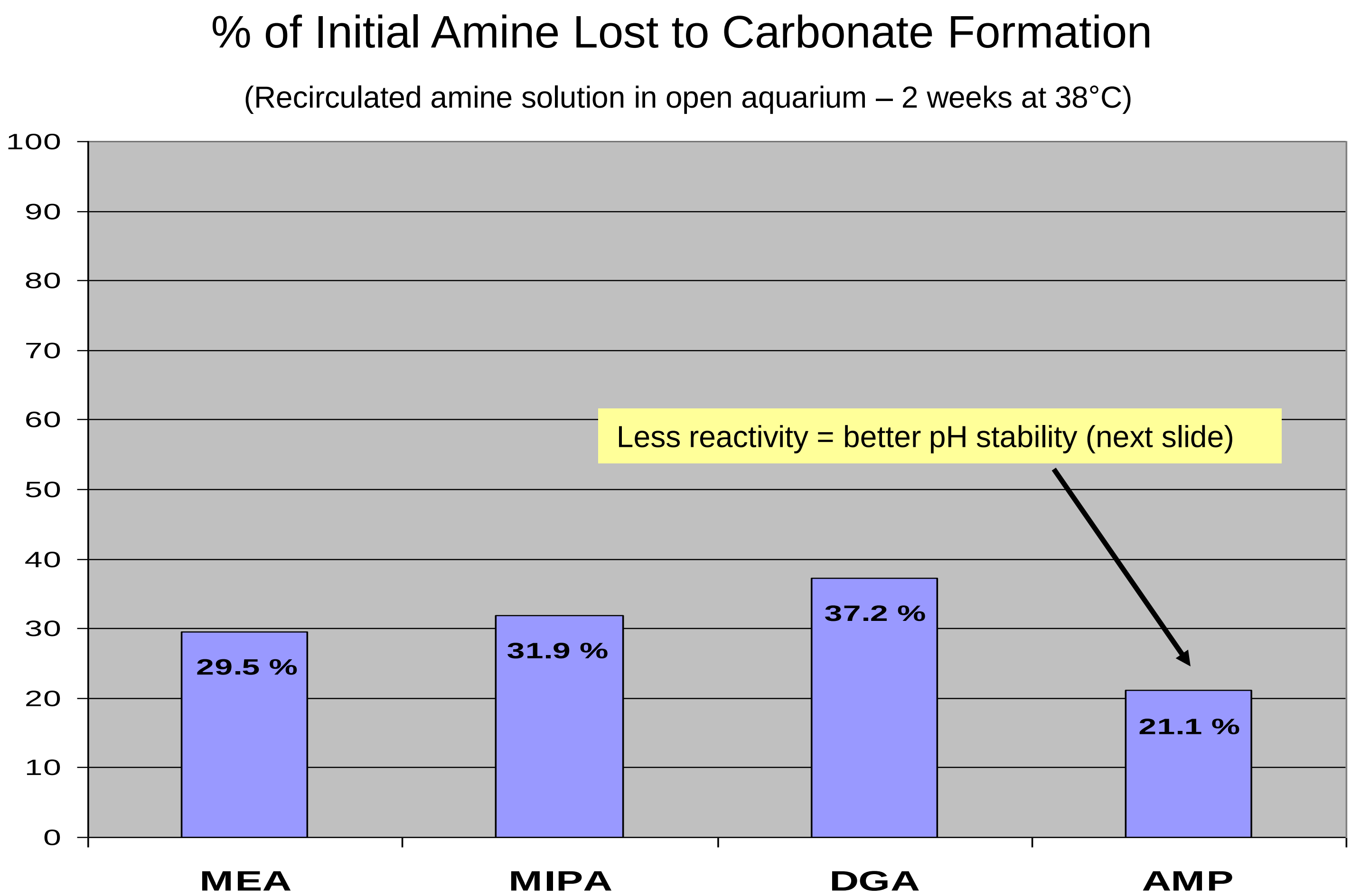
NaOH & KOH = High pKa = Poor Buffers



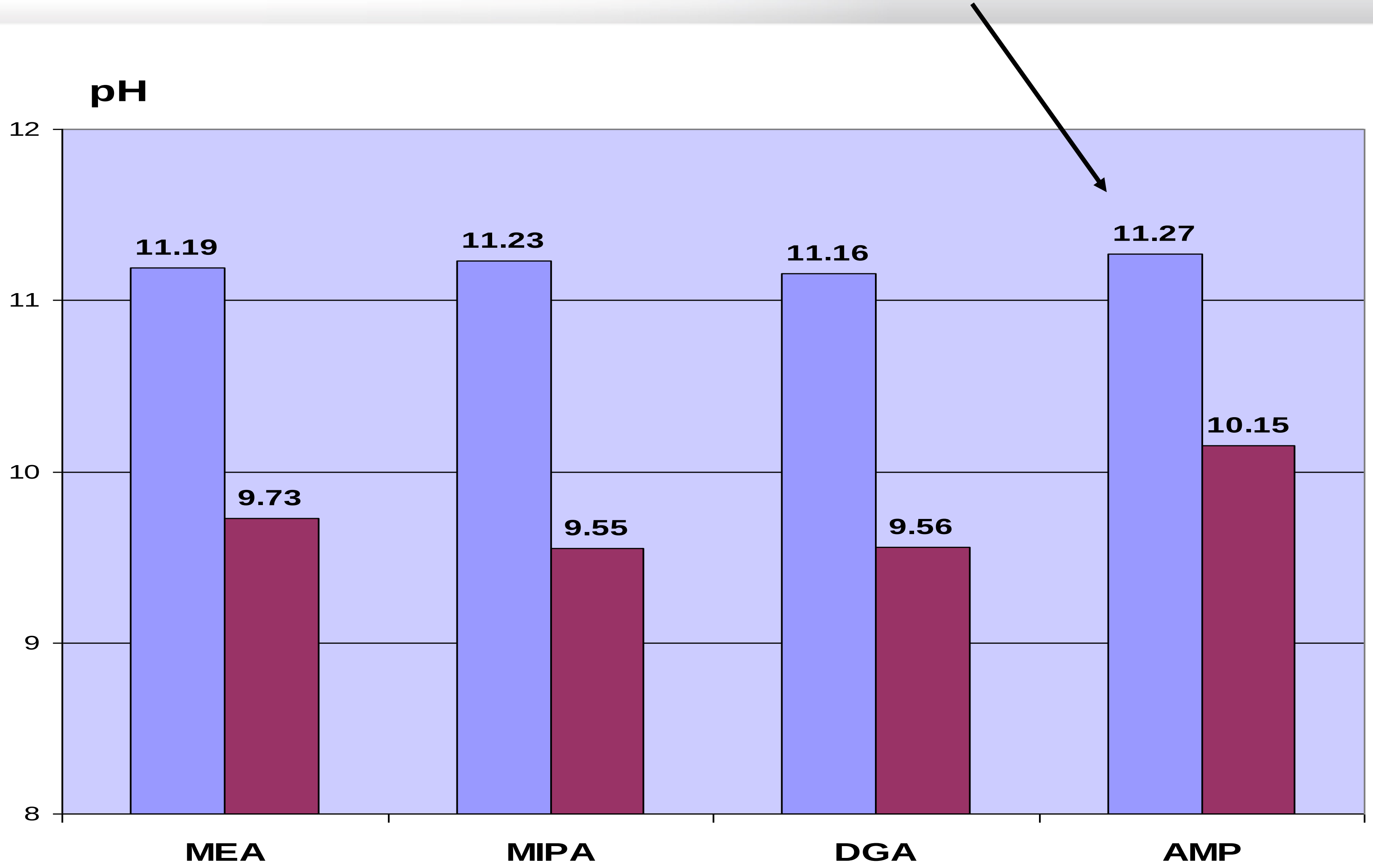
Amines = Low/Med. pKa = Better Buffers



Reactivity with Atmospheric CO_2



Lower CO_2 Reactivity = Better pH Stability



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Secondary Benefits

- Some amines significantly enhance the performance of registered biocides
  - Better control of bacteria & fungi
  - Better pH stability <u>even with lower reserve alkalinity</u>
  - Better maintenance of iron/steel corrosion control
  - Less aggressive on aluminum alloys

- Example
  - Partial replacement of TEA with much lower levels of OA

Synthetic MWF Formulation

Ingredient	MEA/TEA	OA/MEA/TEA
Dicarboxylic Acid	3%	3%
Inversely Soluble Ester	8	8
Phosphate Ester	3	3
OA	**--**	**4**
TEA	**15**	**4**
MEA	**5**	**5**
Triazine	**2**	**2**
Deionized Water	64	71
Total	100	100
Total Alkalinity (moles amine/100 lbs fluid)	**83**	**60**

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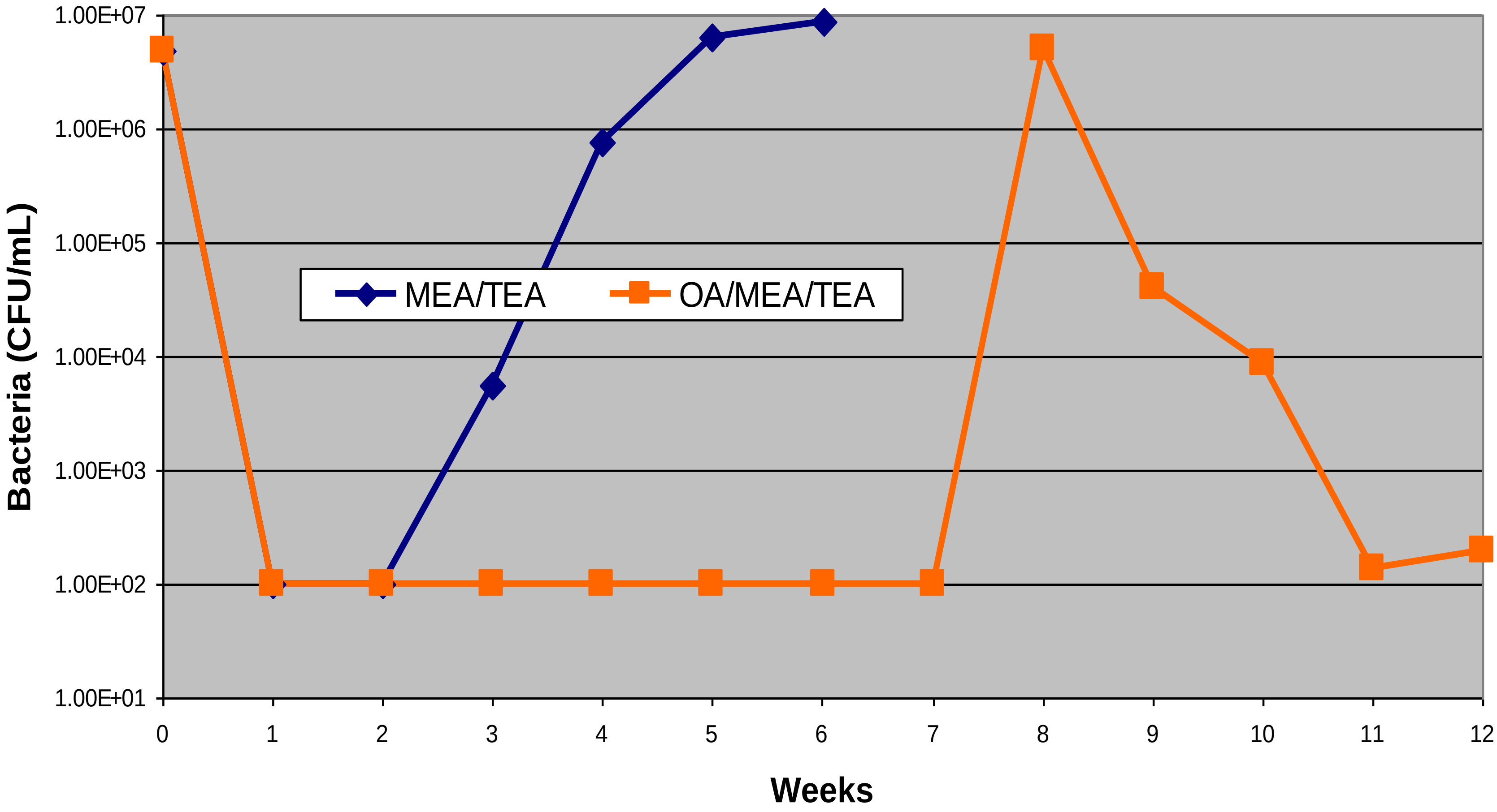
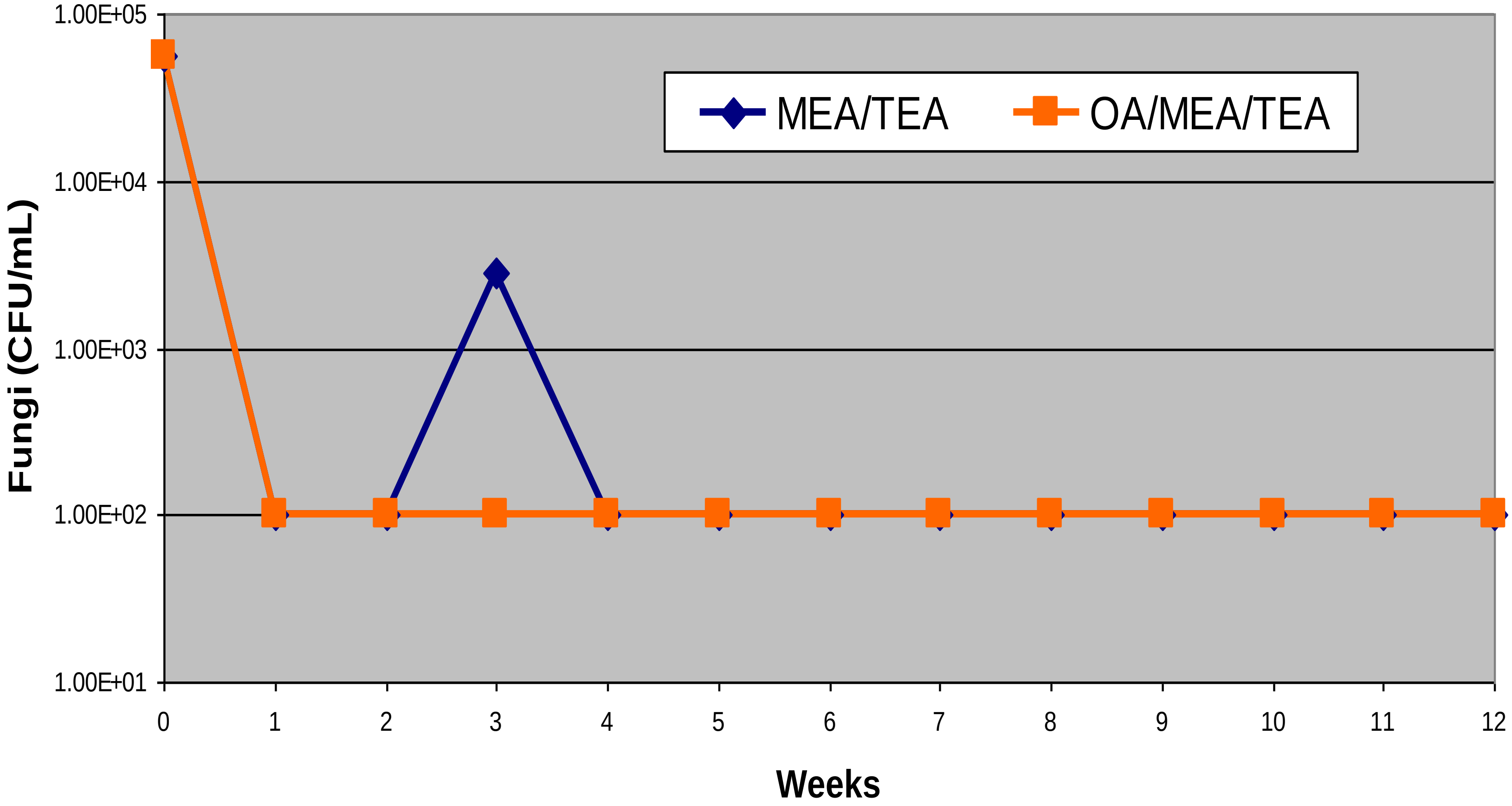
Bacterial Control*



* Weekly inoculation 10E6 CFU/mL bacteria, 10E4 CFU/mL fungi

Fungal Control*



* Weekly inoculation 10E6 CFU/mL bacteria, 10E4 CFU/mL fungi

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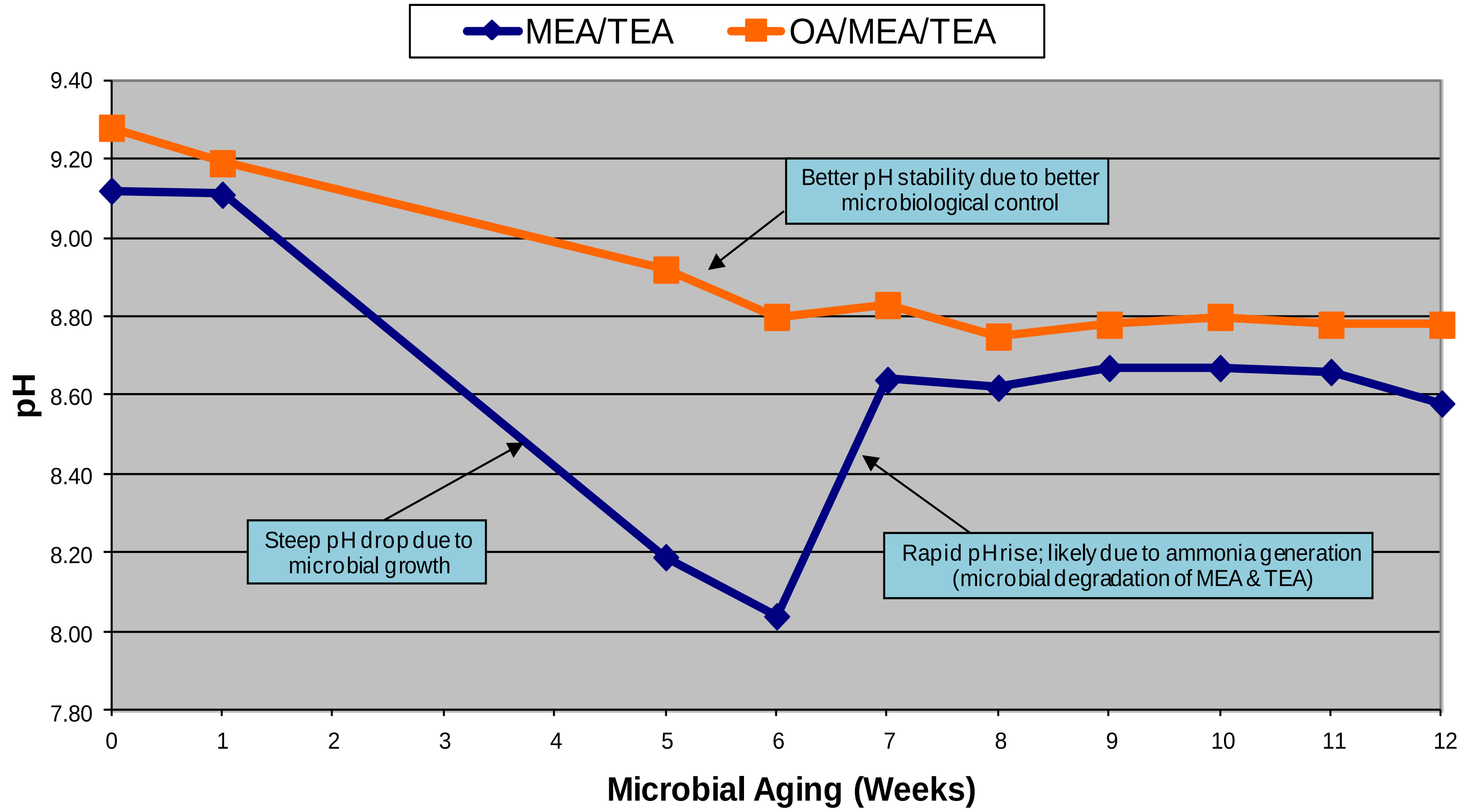
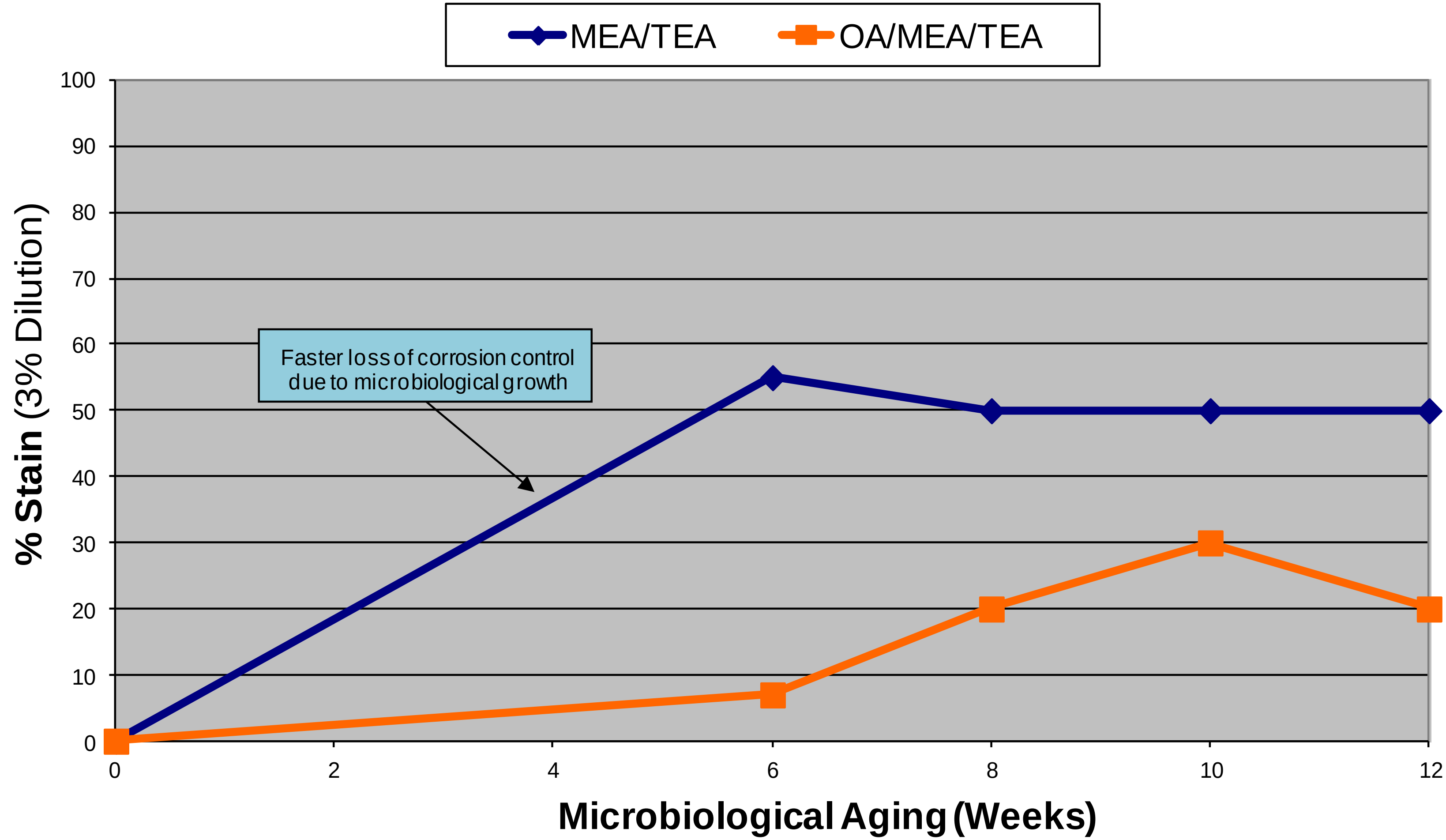
pH Control



MEA/TEA
OA/MEA/TEA
9.40
9.20
9.00
8.80
8.60
8.40
8.20
8.00
7.80
pH
0
1
2
3
4
5
6
7
8
9
10
11
12
Microbial Aging (Weeks)
Better pH stability due to better microbiological control
Steep pH drop due to microbial growth
Rapid pH rise; likely due to ammonia generation (microbial degradation of MEA & TEA)

Corrosion Control



Secondary Benefits: Conclusions

- Good microbial control is critical
- Controlling microbes prevents formation of "bad acids"; a high level of reserve alkalinity isn't needed
- TEA is an ideal pH buffer for MWFs but is susceptible to biological attack; buffering ability is rapidly lost
- Ammonia generation due to biodegradation of ethanolamines can fool operators into thinking pH is under control

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Health, Safety & Regulatory Factors

- Strong bases are hazardous to handle (KOH, NaOH)
- Secondary amines (DEA, DIPA, BEA) are regulated in Germany (TRGS 611) due to possible formation of nitrosamines
- Ammonia formed by biodegradation of certain amines can result in sudden release during tank-side pH adjustment
- Some amines (TEA, others) can leach high levels of cobalt during carbide tool production; possible adverse health effects if leaching inhibitors (tolyltriazole, etc.) aren't present

Questions?

Thank You!