QUANTITATIVE RANKING MEASURES OIL FIELD CHEMICALS ENVIRONMENTAL IMPACT

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ABSTRACT

Environmental stewardship has been and continues to be a critical component of the oil and gas industry, as exploitation of shale and other unconventional gas reservoirs requires large volumes of water for economic and efficient production.

Evaluating and communicating the hazards of chemicals is done in a highly variable manner across the world. However the recent adoption of the Globally Harmonized System of Classification and Labeling of Chemicals (GHS) by multiple Global regulatory bodies has brought international consensus to hazard criteria and definitions. This system is being implemented with REACH in the EU. In the US OSHA has just proposed the GHS criteria as the basis for modifying their hazard communication regulations. This standardization ensures information about hazards and toxicity of chemicals is more universally available, to enhance protection of human health and the environment during handling, transportation and use. It is this scheme that we are beginning to utilize as the basis for the ranking of products and systems.

This paper will describe the evaluation and implementation of a practical and quantitative process of ranking well servicing products based on their safety, health and environmental impacts. The ranking allows operators to select and use products that best fit their environmental stewardship goals, and provides scientifically sound tools for better research and development, and educational efforts.

INTRODUCTION

High-volume, high-rate hydraulic fracturing and horizontal drilling have unlocked vast potential reserves of natural gas in North America and throughout the world. However, as with most industrial efforts or processes, shale gas and oil exploitation does not come without manageable risks. In this case there is the concern of managing the depletion of valuable natural resources such as fresh water. This concern includes the perceived potential risk that chemicals used in the fracturing process could enter underground safe drinking water (USDW) reservoirs.

Extensive studies of hydraulic fracturing by the United States Environmental Protection Agency (EPA, 2004), independent interstate advocacy groups such as the Ground Water Protection Council, the Interstate Oil and Gas Compact Commission and state regulatory agency-sponsored studies (NY Department of Environmental Conservation, 2009) have found that hydraulic fracturing does not pose an unreasonable risk to subsurface drinking water supplies.

Nevertheless, oil and gas companies, responsible for the development and transmission of natural gas to the market place are always seeking to utilize increasingly safer, technologies in oil and gas operations, including chemical application during hydraulic fracturing. However, current environmental guidelines for hydraulic fracturing in the United States are based predominately upon well construction controls and evolving state regulatory requirements.

This paper documents a methodology to identify, develop, test and implement a well services chemical ranking system that is transparent, qualified by environmental experts and based upon a broadly adopted, globally applicable chemical hazard evaluation system. The system design requirements included:

- **Credibility** in terms of the criteria and rationale used for the ranking
- **Transparency** for easy explanation to stakeholders such as customers or regulators
- **Scientific soundness,** with a documented basis for criteria and ranking of each hazard
- **Validity,** based as much as possible on existing systems and criteria
- **Practicality,** considering the range of chemicals used in well service products, the profile of the suppliers, and the data normally available for these chemicals
- **Quantitative** to indicate relative, or scaling of, “greenness”

The authors caution that “green” or environmental preferred products or system claims should be validated with sound, scientific criteria.

OVERVIEW OF EXISTING SYSTEM

To satisfy the above criteria, the existing processes and systems for evaluating or approving chemical products as “green” were studied. It was immediately clear when doing this that the content and terminology used for such systems is highly variable. The word “green” has many definitions and the criteria for evaluating “acceptability” of a product is equally diverse. Some examples of the schemes reviewed and their attributes are included in **Table 1**. The existing schemes are administered by a wide range of organizations including governments, private non-profit organizations and private for-profit organizations. “Green” evaluations and environmental certification programs have proliferated in recent years.

Estimates indicate there are about 600 labeling schemes or environmental labels worldwide with as many as 80 in the United States. They cover a wide range of categories with many being very specialized and tailored to a specific application or service. Because “green certification” is not a regulated industry, the basis, or criteria, for certifications varies widely. Terms found in the programs include:

- Safer chemicals
- Green chemistry
- Sustainability
- Measurable environmental impact
- Environmentally friendly

The programs range from relative rankings to simple pass/fail criteria. They are generally hazard-based, with some also utilizing exclusionary lists, or prohibited chemicals, as pass/fail criteria. Several of the schemes look at the sustainability attributes of the production process as well as the product. The bottom line is that there is no single definition for “green” and companies have some leeway in defining the attributes to be used for product development and marketing. Part of the problem is a lack of standardized hazard communication systems globally. In the North Sea, under technical guidance from the Centre for Environment, Fisheries and Aquaculture Science (CEFAS) a process and standard for offshore chemical utilizations known as Offshore Chemical Notification Scheme (OCNS) is utilized. Regulated in the UK by the Department of Environment and Climate Change (DECC) and in the Netherlands by State Supervision of Mines (SSM) , the system includes thorough guidelines for chemical evaluation, testing, limitations and documentation, specific to the North Sea marine environment. This system can be considered a model for adoption in other active oil and gas offshore regions; similar systems are in place in other major offshore basins, such as Brazil (Gomez, 2010). However these systems do not include the range of evaluation criteria considered important for onshore activities.

In an effort to unify communication of chemical hazards, the Global Harmonized System for Classification and Labeling of Chemicals (GHS) was developed by the United Nations sponsored Inter-organization Program for Sound Management of Chemicals (IOMC) (United Nations 2003). GHS is a comprehensive approach to:

Defining health, physical and environmental hazards of chemicals;
Creating classification processes that use available data on chemicals for comparison with the defined hazard criteria; and
Communicating hazard information, as well as protective measures, on labels and Safety Data Sheets (SDS)

For many specific hazards, such as acute toxicity or flammability, the GHS system has a defined, data-based scaling set of quantitative criteria that can be applied to indicate relative hazard. Therefore a “ranking” can be accomplished, based on a standard and internationally recognized set of criteria. Examples of the GHS criteria and the resultant ranking numbers are found in **Table 2**.

The European Union will use GHS beginning in December 2010 as the regulatory basis for hazard determination and communication. In the United Sates, the US EPA is using GHS within its Design for the Environment (DfE) program. In addition, the US Occupational Health and Safety Administration (OSHA) has proposed to modify its Hazard Communication standard to utilize many GHS elements. Although the OSHA rules are not expected to be finalized for some time, the hazard determination criteria found in the GHS system are rapidly becoming a standard for hazard classification and communication.

CHOOSING HAZARDS OF INTEREST

In reviewing the existing systems, it became clear that some common hazards are utilized for evaluating how products affect people and their environment. Many systems focus only on environmental impact, while others evaluate a full range of attributes, including human health and physical hazards. Most ranking systems are based on the inherent hazards of the products at "full strength," without taking use conditions or actual exposures into consideration. No one existing system had the breadth of scope desired for this project.

Based on the review of existing systems, however, three distinct sets of hazards were chosen as important for an oilfield products evaluation system:

- Environmental
- Acute/chronic aquatic toxicity
- Bioaccumulation
- Biodegradation
- Priority pollutants
- VOC content

- Physical hazards
- Explosive
- Flammability
- Oxidizer
- Corrosive

- Human Health
- Acute mammalian toxicity
- Irritation/corrosion
- Carcinogenicity
- Genetic toxicity
- Reproductive and developmental toxicity

After choosing the specific hazards to be assessed, it was necessary to select a system of scientifically sound and transparent criteria that could be used to quantify each chemical's hazard level. A variety of such systems are used worldwide, including some that are regulatory and guidance–based, but most are inconsistent in the scaling and criteria used for quantifying hazards.

Adoption of the GHS by multiple global regulatory bodies suggests that it has achieved some level of international consensus for hazard criteria and definitions. Therefore, GHS was chosen to serve as the basis for the ranking of well service products.

To enable product ranking, a spreadsheet application was created. For each hazard criteria above, a scoring scheme was devised based on quantitative GHS criteria where available, or simple pass/fail evaluation. In most cases, each hazard is rated on a scale of 0 to 3 with equal weighting, but the ranking tool allows weighting of a score if a particular hazard is considered more or less important than the others. Using chemical data and these hazard ratings, then, a score for the three sets of hazards (environmental, physical and human health) is generated, with individual and/or aggregate rankings. See **Table 2** for examples of scoring criteria.

DATA GATHERING

Having established the criteria for product assessment, data gathering began with reviewing Safety Data Sheets for a number of oilfield products. Several challenges became clear almost immediately—necessitating expansion of the task. First, a fully compliant OSHA-mandated SDS in the US is likely to have significant gaps in the data needed for the new ranking system. Specifically:

OSHA SDS requires no environmental information.

If all the components of a product are classified by OSHA as non-hazardous, the SDS needs no specific substance identification. However, OSHA's "non-hazardous" classification does not account for potential environmental hazards, and if the SDS does not identify a specific substance, no database searching can be accomplished for environmental data.

Little data was available for most of the mixtures (i.e., products made from a combination of chemicals). Mixture data was generally available for physical hazards, but for most health and environmental hazards, the ranking process had to combine data for individual component chemicals, with the weight percentage contribution of the individual components used to calculate the overall score.

Much of the necessary but missing data (including names of specific constituent chemicals) was considered "proprietary" or "trade secret" by the chemical supplier. To obtain the data needed for this project, chemical suppliers were asked to execute nondisclosure agreements with an outside consultant and provide specific information and data that was not included on the SMS forms. The consultant then used the additional information to complete the evaluation and provide results in a manner that protected the confidentiality of the product formulas (for example, see Table 3).

In cases where the supplier had the name of the chemical but not all of the information required for hazard quantification, a database option was used. If a CAS® (Chemical Abstract Services) registry number (American Chemical Society, 2009) or other specific chemical identity is available, a number of reliable databases can provide hazard data. For this project, a standard protocol for searching was developed and was generally successful in filling data gaps for individual chemical components.

If no data could be found from any of these sources, a default value of “1” was used in the spreadsheet application. In some cases, a scientific assessment could be done utilizing the “read across” or quantitative structure-activity relationship (QSAR) approach (Selassie, 2003). This requires some time and effort and was done on a prioritized basis where a particular hazard was considered essential to evaluate the product.

PRACTICAL LESSONS LEARNED

Oil & gas services use a wide variety of chemicals. Even with a comprehensive evaluation system, interpreting results can be complicated. Examples of lessons learned include:

A system that evaluates the inherent hazard of chemicals does not account for use conditions or exposure scenarios. These considerations must be made after the relative rankings are calculated. The dilution factors applied on site or downhole are a legitimate part of any risk assessment for chemical use but are difficult to incorporate in a large-scale greenness ranking process.

> Well service products are normally used at very low concentrations, typically applied in aqueous fluid systems at volumetric concentrations on the order of 0.1%. All of the chemicals combine to create a final system with chemical concentration generally less than 0.5%.
>
> Nevertheless, from the outset, it was decided to evaluate the relative greenness of products in their concentrated form, as transported to the wellsite. It is generally accepted that the risk is greatest when the product is in this form, with potential exposures to the environment through surface spills and human exposure while managing the dilution process at the wellsite.

Evaluating the concentrated product does not take into account the relative efficiency of the product. This can be apparent when comparing products of the same family (e.g., surfactants), or of the same chemistry (e.g. different dilutions of the same product). Hence, situations can arise where the required concentration of a product in a system belies its low initial hazard ranking. Conversely, less green products may be preferred if their efficiency allows their use at lower concentrations than greener products.

Evaluating the relative hazards of a dilute fracturing fluid or other stimulation fluid system can guide decision-making, even though the numerical scores are orders of magnitude higher than would apply for dilute systems as they would be used in the field.

Applicability of the environmental and health hazard criteria to solid, inorganic substances requires careful consideration that is also impacted by form of use or handling. For example, the inherent hazard ranking of proppant or sand based on silica content can give a relatively high ranking due to its short-term inhalation risk, which is totally unrelated to the product’s ultimate and long-term use underground in a hydraulic fracture.

Because the biodegradation endpoint is generally not applicable for inorganic substances, these substances are scored as “0” for this criterion.

EXAMPLE OF EVALUATION/RANKING SYSTEM

The following provides examples of product evaluation within performance categories or frac systems. As explained earlier, to overcome issues related to “trade secret” or “proprietary” chemical content associated with third-party chemistry, qualified environmental consultants facilitated communication with third-party providers, gathered data and performed final scoring.

A. Product evaluation

An example of a surfactant product evaluation is given in **Table 3.** This example demonstrates the degree of product formulation confidentiality that is maintained between the chemical supplier, consulting environmental analyst and the final user (service company). It also demonstrates how specific hazards can be quickly identified

– thus allowing targeted efforts for reduction in future product development.

B. Product categories

An evaluation of the relative greenness of several surfactant products is shown in **Table 4**. This report format permits quick identification of the preferred product in a particular product category, or the best product with respect to a particular hazard category. Note that this comparison does not account for product effectiveness or product concentration, and if these parameters differ among the products in question, some attempt must be made to normalize the product scores.

C. Frac fluid systems comparison

Fluid systems can be evaluated in two ways. The first shows system component hazard scores, allowing quick identification of components that, if replaced by better alternatives, would lead to a better system score. A second displays all system hazard scores for similar or dissimilar fluid systems, for quick comparison. As noted previously, when comparing fluid systems, it is important to consider fluid system *performance* (e.g., efficiency, cleanup, proppant transport, etc.), which is complicated to normalize. Two example fluid systems are shown in **Table 5**, with weighting applied to system components according to typical field application, but no overall system weighting for "performance."

CONCLUSIONS

1. The environmental hazard ranking system has global applicability.
2. It offers a standardized ranking process with transparency to client, federal, state or local regulatory bodies.
3. The approach and system have been independently developed with expert environmental validation.
4. The system can rank individual products within a category and complete systems (frac, cement, acid, etc.)
5. The system honors intellectual property and free-market practices.
6. The system simplifies product support/retirement prioritization initiatives.
7. The system provides validation to support marketing claims.
8. The system supports R&D and suppler interaction for 'green' product development.

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Table 1
Examples of environmental schemes and their attributes

Type	Description	Process
Design for the Environment (DfE) / CleanGredients Untied States	DfE engages partners to use the EPA's tools and expertise to help industry move to adopt safer chemicals. DfE has a number of programs including: safer electronics, safer flame retardants and safer formulations. By forming partnerships with the DfE Program, formulators can take part in an important national effort to improve the human health and environmental profile of chemical-based products, which will benefit the quality of aquatic life and the environment, the biodegradability of waste streams, and human health and safety. DfE uses hazard-based criteria to determine acceptability of an ingredient or formulation.	The criteria can be found at http://www.epa.gov/dfe/pubs/projects/formulat/saferproductlabeling.htm Third parties review ingredient data for acceptability against the criteria. Acceptable products are listed on CleanGredients website (http://www.cleangredients.org) 1) US EPA sets the criteria. 2) Current approved third party reviewers are NSF and ToxServices. 3) CleanGredients was developed by the GreenBlue Institute (http://www.greenblue.org)
ECOCERT Europe	Standards are based on the use of renewable origin ingredients (favoring the use of ingredients produced by Organic Farming) and obtained by processes "respectful of the environment." Most synthetic ingredients are prohibited. Audits are conducted by Ecocert at manufacturing, packaging and distribution sites.	Application forms for cosmetics can be found at http://www.ecocert.com/List-of-the-available-documents.html and a description of the process for detergents can be found at http://www.ecocert.com/Les-etapes-de-la-labellisation-en.html ECOCERT
Green Seal United States	Green Seal works with manufacturers, industry sectors, purchasing groups, and governments at all levels to "green" the production and purchasing chain. A life-cycle approach is utilized. This means Green Seal evaluates a product or service beginning with material extraction, continuing with manufacturing and use, and ending with recycling and disposal. Products only become Green Seal certified after rigorous testing and evaluation, including on-site plant visits. Green Seal uses hazard-based criteria to determine the acceptability of a formulation. Also certain ingredients are banned in the different standards. For example, ethoxylated compounds (including ethoxylated alcohols) are not allowed in personal care products).	Application forms can be found at http://www.greenseal.org/certification/forms_fees.cfm Green Seal
EcoLogo Canada	EcoLogo provides customers – public, corporate and consumer – with assurance that the products and services bearing the logo meet stringent environmental standards that have been verified by a third party auditor. The standards are designed such that only the top 20% of products available on the market can achieve certification. Criteria are hazard-based and list-based (banned ingredients).	The criteria for the different groups can be found at http://www.terrachoice-certified.com/en/criteria/search/ The application procedure can be found at http://www.terrachoice-certified.com/en/certified/applyonline/ TerraChoice (www.terrachoice.com) is currently managing the program
EU Eco-label (The Flower) Europe	Established in 1992, the EU Eco-label "Flower" is a certification scheme aimed to help European consumers distinguish "greener", more "environmentally friendly", products and services (not including food and medicine). All products bearing the "Flower" have been checked by independent bodies for complying with ecological and performance criteria. Criteria have been established for 23 groups and are reviewed every 3 years. Ecolabel criteria are not based on one single factor, but on studies which analyze the impact of the product or service on the environment throughout its life-cycle, starting from raw material extraction in the pre-production stage, through to production, distribution and disposal.	Criteria for the different groups can be found at http://ec.europa.eu/environment/ecolabel/ecolabelled_products/product_categories_en.htm The application procedure is described at http://ec.europa.eu/environment/ecolabel/ecolabelled_products/application_procedure_en.htm European Eco-labeling Board (EUEB) develops the criteria. Competent Bodies manage the applications.

Table 2
Example of GHS criteria and ranking numbers

Environmental Criteria

Scoring	0	1	2	3
Acute/chronic Aquatic Toxicity	>=100 ppm	>10 ppm and <100 ppm	>1 ppm and <= 10 ppm	<= 1 ppm
Air Pollutants (VOCs?)	no			yes
Priority water pollutants	no			yes
Bioaccumulation*	no	1000	2000	5000
Biodegradation	readily degradable- conversion to CO2 after 28 days (OECD 301F) and a half-life of < 180 days^	Meets 10 day window Criteria in biodegradation test (60% conversion to CO2)	Inherently degradable- slow degradation apparent but does not meet ready biodegradation criteria	not biodegradable or produces degradation products of concern

* values based on REACh (2000, 5000 and US EPA 1000)

^ and not produce degradation products of concern

Acute Toxicity

Scoring	3	2	1	0
Exposure route	Category 1	Category 2	Category 3	Category 4
Oral (mg/kg bodyweight) see: Notes (a)(b)	≤ 5	>5 and ≤ 50	>50 and ≤ 300	>300 and ≤ 2000
Dermal (mg/kg bodyweight) see: Notes (a)(b)	≤ 50	>50 and ≤ 200	>200 and ≤ 1000	> 1000 and ≤ 2000
Inhalation -Gases (ppmV) see: Note (a) Note (b) Note (c)	≤ 100	>100 and ≤ 500	>500 and ≤ 2500	>2500 and ≤ 20000
Inhalation -Vapors (mg/l) see: Note (a) Note (b) Note (c) Note (d)	≤ 0.5	>0.5 and ≤ 2.0	>2.0 and ≤ 10.0	>10.0 and ≤ 20.0
Inhalation – Dusts and Mists (mg/l) see: Note (a) Note (b) Note (c)	≤ 0.05	>0.05 and ≤ 0.5	>0.5 and ≤ 1.0	>1.0 and ≤ 5.0

* from GHS

Table 3
Product evaluation Surfactant A

Component	Methanol	Component A	Component B	Water	Total Score	Weight Score
CAS Number	67-56-1	CAS# A	CAS# B	7732-18-5		
%	x	x	x	x		
Environmental Criteria						
Acute Aquatic Toxicity	1	3	2	0		
Air Pollutants (VOCs)	3	0	0	0		
Priority Water Pollutants	0	0	0	0		
Bioaccumulation	0	0	0	0		
Biodegradation	0	1	1	0		
total score/component	x	x	x	x	176	**4.4**
Toxicological Criteria						
Acute Mammalian Toxicity	0	0	0	0		
Carcinogenicity	0	0	0	0		
Genetic Toxicity	1	1	0	0		
Reproductive and Developmental	3	3	3	0		
Corrosive/Irritant	1	1	1	0		
total score/component	x	x	x	x	223	**5.6**
Physical Hazards						
%					100	
Explosive					0	
Flammable					1	
Oxidizer					0	
Corrosive					0	
total score					100	**2.5**
Product Score (Environmental, Toxicological and Physical Hazard Criteria)					499.0	**12.5**
						(out of 100)
Data gap = 1						

Table 4
Surfactant comparison

Surfactant Product	A	C	D	E	F	G	H
Environmental Criteria	4.4	4.1	2.9	4.4	3.7	3.1	1.4
Toxicological Criteria	5.6	6.6	4.1	6.8	2.2	3.7	3.9
Physical Hazards	2.5	5.0	0.0	2.5	0.0	2.5	0.0
Product Score	**12.5**	**15.7**	**7.0**	**13.7**	**5.9**	**9.3**	**5.3**

worst case	
best case	

Table 5
System comparison

System A (Slick-water)	Density (gm/cm^3)	Concentration (gpt/ppt*)	Product score	Weighted product score
Friction Reducer	1.06	1	9.1	9.6
Surfactant	1.18	2	5.3	12.5
Clay Control	1.10	1	3.8	4.2
Biocide	1.36	0.05	15.0	1.0
			Total System Score x 1000	**27.4**

System B (Cross-linked)	Density (gm/cm^3)	Concentration (gpt/ppt*)	Product score	Weighted product score
Gellant*	n.a.	30	2.5	9.0
Buffer*	n.a.	5	2.5	1.5
Buffer	1.40	0.5	3.4	2.4
Cross-linker	1.13	1	1.8	2.0
Breaker*	n.a.	2	5	1.2
Surfactant	0.97	1	13.3	12.9
Clay Control	1.10	1	3.8	4.2
Biocide	1.36	0.05	15	1.0
			Total System Score x 1000	**34.2**

gpt = gal per thousand gallons (liquid)
ppt* = lbs per thousand gallons (solid)