

# Arsenic Adsorption by Some Iron Oxide Minerals: Influence of Interfacial Chemistry\*

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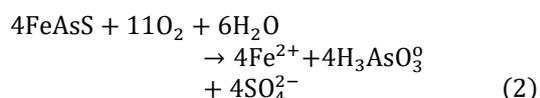
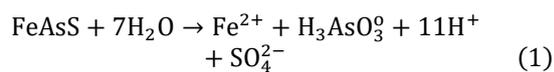
## Abstract

The dramatic increase in hydrometallurgical extraction of gold from arsenic bearing gold ores has inevitably resulted in the release of arsenic into the environment worldwide. Residual arsenic minerals in tailings storage facilities can be oxidised and mobilise arsenic into the environment. This can contaminate soils, ground and surface waters and eventually biota. In spite of well-established technologies and recent advances in arsenic remediation, there are limited knowledge and understanding of the iron oxide substrate (goethite, hematite and magnetite) mineralogy and the fate of arsenic on the surface charge of these iron oxide substrates in an aqueous media during adsorption. The aim of the present study was to investigate the influence of interfacial chemistry on arsenic adsorption onto selected iron oxide particles to assist in developing a better understanding and new knowledge in arsenic removal from contaminated waters. Bulk mineralogy and partial chemical composition of selected iron oxide minerals were obtained using quantitative x-ray diffractometry (QXRD) and acid digestion followed by metal determination using inductively coupled plasma optical emission spectrometry (ICP-OES) respectively. Zeta Potential measurements involving iron oxide particles as arsenic adsorbents were carried out to elucidate the influence of interfacial chemistry on the adsorption behavior of arsenic from solution. The study confirmed that the iron oxide minerals were predominantly hematite, magnetite and goethite with goethite containing significant amounts of quartz. Arsenic adsorption was pH dependent and strongly influenced the zeta potential and isoelectric point (IEP) of the iron oxide particles. The zeta potential of all substrates studied was strongly positive at pH 2 but indicated a reversal at pH ~ > 9. The interaction between substrates, arsenic and its hydrolysable products resulted in significant decrease in the magnitude of zeta potential and change in IEP indicating specific adsorption.

**Keywords:** Arsenic, Adsorption, Iron Oxide Minerals, Zeta Potential

## 1 Introduction

Arsenic can be introduced into the geo-environment because of the weathering of arsenic bearing minerals. For instance, refractory ores must be pretreated to decompose the sulphide minerals for effective recovery. However, residual undecomposed material in the tailings can weather to mobilise heavy metals into the geo-environment (Warhurst and Noronha, 2000; Fan *et al.*, 2016). Arsenopyrite oxidation involves iron, sulphur and arsenic. It has been shown via activation energies that arsenopyrite oxidation occurs through surface reactions (Lengke, and Tempel, 2005). Therefore, in the presence of oxygenated water arsenic is released from the arsenopyrite as As (V) or metastable As (III). In arsenopyrites, Craw *et al.*, (2003) and Walker *et al.*, (2006) suggest that As(1-) and As(0) oxidise to As(III) at pH 4-9 as shown in Equations 1 and 2 respectively.



Furthermore, during the bio-oxidation of auriferous sulphides, arsenic laden effluent is normally neutralised and deposited in tailings dams. The

seepage from sulphide waste rocks and the precipitated arsenic materials in tailings dams can be mobilized into the geo-environment. Thus, it is important to remediate arsenic migration into the environment.

Several authors have demonstrated the usefulness of iron oxides as good adsorbents for arsenic remediation from water (Raven *et al.*, 1998; Dixit and Hering, 2003; Yavuz *et al.*, 2006; Giménez *et al.*, 2007; Shipley *et al.*, 2009; Koomson and Asiam, 2013). Arsenic (V) adsorption capacity of 37.3 mg/g by goethite (Faria *et al.*, 2014), 46.06 mg/g by magnetite (Feng *et al.*, 2012) and 95 mg/g by hematite (Prucek *et al.*, 2013) have been reported in the literature. However, there is limited knowledge and understanding of the iron oxide substrate mineralogy and the fate of arsenic on the surface charge of the substrate in an aqueous media during adsorption. Obtaining an in-depth understanding of the substrate mineralogy and the fate of arsenic on the substrate's surface charge during adsorption will assist in the long-term storage and management of the substrates after adsorption. Hence, this is the focus of the study.

## 2 Resources and Methods Used

### 2.1 Materials

In this research, three different types of iron oxide minerals (goethite, hematite and magnetite) were

used for the investigations. The iron oxide minerals: goethite, hematite and magnetite were obtained from Wards natural science (geology study pack), Hibbing, Minnesota, USA, Australia Bulk Minerals, Adelaide, Australia and Arrium Mining and Materials, Australia, respectively. Samples were used as received.

All chemical reagents used in the investigation were of analytical grade and obtained directly from commercial suppliers. Potassium hydroxide and nitric acid were used to control pH whilst potassium nitrate was used to control the ionic strength in the adsorption experiments. Arsenic (V) stock solution was obtained from Adela Scientific, Australia.

## 2.2 Methods

### 2.2.1 Materials Characterisation

Bulk mineralogy of iron oxide minerals used in this work was determined by using quantitative x-ray diffractometry (QXRD; Phillips PW 1050 X-ray generator equipped with Sietronic automated data collection). The specific surface area of the mineral particles was analysed by using Brunauer, Emmett and Teller (BET) method (Brunauer et al., 1938). The Gemini VII 2390 (Micrometrics, USA) was used. Partial chemical analysis of the minerals was determined using acid digestion. A known mass of each sample (3 g of  $\sim 75 \mu\text{m}$ ) was digested and refluxed with a mixture of acids including hydrofluoric, nitric, perchloric and hydrochloric acid. Elements in supernatant solutions were then analysed using inductively coupled plasma optical emission spectrometry (ICP-OES; Perkin Elmer 5300 DV).

### 2.2.2 Comminution

The as received iron oxide minerals were wet milled for 20 mins each by using a rod mill with a solid loading of  $\sim 1864 \text{ g}$  (1000 g mineral and 864 g mill rods) and 1 L de-ionised water to obtain a particle size range of 80% passing  $10 \mu\text{m}$  required for zeta potential measurements. As a precaution to prevent contamination, stainless steel coated milling rods were used in this study.

### 2.2.3 Zeta Potential Measurement

Zeta potential measurements were conducted to investigate and ascertain the effect of arsenic adsorption on the surface charge of the iron oxide minerals. In this work, the mineral particle zeta potential was determined from dynamic mobility measurement using an acoustosizer (Acoustosizer II, Colloidal Dynamics, Inc, Australia).

Zeta potential measurements were conducted on 8 wt% (280 ml) agitated suspensions of goethite,

hematite and magnetite particles dispersed in  $1 \times 10^{-3} \text{ M KNO}_3$ . The  $1 \times 10^{-3} \text{ M KNO}_3$  background electrolyte was used to avoid the effects of anomalous surface conductance on the mineral particle surface chemistry prior to arsenic adsorption. Agitation rates between 400 and 1800 rpm were employed. The experiment was conducted at room temperature and the pH was continually monitored in situ using probes, attached to the instrument. Prior to the zeta potential measurements, the suspensions were conditioned for 1 h to ensure even and adequate particle dispersion. During measurements, the suspensions were also allowed to equilibrate at an interval of 5 min before subsequent pH and zeta potential measurements were taken to ensure accurate results.

The pH at which the zeta potential of a mineral particle's surface is zero is known as its isoelectric point (IEP). The IEP is dependent on a number of factors including sample origin/mineralogy, type of electrolyte background used, measurement procedure employed and whether some other chemical specie(s) is being adsorbed onto the mineral particle's surface.

To be able to explain the changes in the surface chemistry of goethite, hematite and magnetite during As adsorption, an indifferent background electrolyte ( $1 \times 10^{-3} \text{ M KNO}_3$ ) was first used for the zeta potential analysis to ascertain the initial IEP and zeta potential magnitude of the mineral surface. Afterward, a concentration of 20 ppm ( $2.67 \times 10^{-4} \text{ M}$ ) arsenic was then introduced and the zeta potential was measured to enhance the identification of any changes in the interfacial properties of the mineral surface used.

Before all measurements, the acoustosizer was calibrated using dissolved potassium tungstosilicate ( $\text{K}_4(\text{SiW}_{12}\text{O}_{40})$  salt as a calibration standard. This was used because it has very high chemical stability and provides a very strong electroacoustic signal.

## 3 Results and Discussion

### 3.1 Mineralogical and Chemical Characteristics of Iron Oxide Minerals

Results of the mineralogical and partial chemical composition of the iron oxide minerals are presented in Tables 1 and 2.

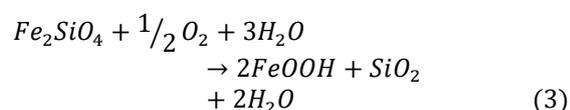
**Table 1 Mineralogical Composition of Iron Oxide Minerals Applied in the Adsorption Process**

A. Goethite	
Compound Name	Composition (wt%)
Iron oxide hydroxide (FeOOH)	51
Silicon oxide (SiO <sub>2</sub> )	34
Iron oxide (Fe <sub>2</sub> O <sub>3</sub> )	12
Potassium, manganese, oxide hydrate (K <sub>0.3</sub> Mn <sub>0.9</sub> O <sub>2</sub> )(H <sub>2</sub> O) <sub>0.4</sub>	3
<b>Total</b>	<b>~ 100</b>
B. Hematite	
Compound Name	Composition (wt%)
Iron Oxide (Fe <sub>2</sub> O <sub>3</sub> )	100
<b>Total</b>	<b>~ 100</b>
C. Magnetite	
Compound Name	Composition (wt%)
Iron oxide (Fe <sub>3</sub> O <sub>4</sub> )	82
Iron oxide (Fe <sub>2</sub> O <sub>3</sub> )	18
<b>Total</b>	<b>~ 100</b>

**Table 2 Partial Chemical Composition of Iron Oxide Minerals**

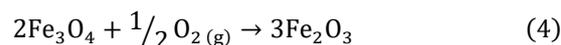
Element	Mineral / Elemental Composition (wt%)		
	Goethite	Hematite	Magnetite
Al	3.53	1.45	0.12
Ca	0.03	0.10	0.95
Fe	46.3	63.50	65.00
Mg	0.20	0.03	0.58
Mn	0.20	0.04	0.075
Si	7.81	1.13	2.23
Ti	0.23	0.03	0.02
S	0.04	<0.01	0.02

The results of the composition of goethite is presented in Table 1 A. It can be seen that the goethite is weathered. It consists of 51% iron oxide hydroxide, 34% silica and 12% hematite as the major constituents. The presence of SiO<sub>2</sub> suggests that the sample has undergone some weathering process. Typically, goethite can be formed from the oxidation and hydrolysis of fayalite as indicated in Equation 3 (Cornell and Schwertmann, 2003).



This indicates that goethite will be highly amenable to comminution. Since goethite is an intermediate oxidation product, it is rarely found in nature in the pure form.

The results of the composition of the hematite is presented in Table 1 B. The results show that the hematite is not weathered. Hematite is an end product of iron mineral oxidation, and hence, can be found pure in geo-materials. The formation of hematite may be due to the oxidation of magnetite as shown in Equation 4 (Lemos *et al.*, 2007).



The composition of magnetite is presented in Table 1 C. It can be seen that the sample contains 82% magnetite and 18% hematite. The composition suggests that the sample is undergoing weathering according to Equation 4.

The results of the partial chemical composition (Table 2) of the iron oxide minerals confirmed the predominance of iron in all three minerals investigated. The minor elements found were Si and Al while Mg, Mn, Ca, Ti and S were in trace amounts.

### 3.2 Specific Surface Area of Iron Oxide Minerals

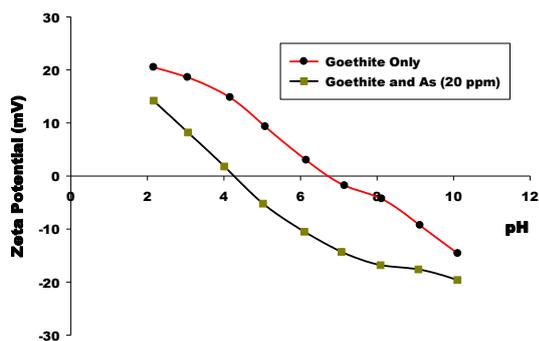
The results of the specific surface area for the iron oxide minerals are presented in Table 3. The specific surface area of the magnetite was 2.79 m<sup>2</sup>/g and that of goethite and hematite were 13.30 and 6.45 m<sup>2</sup>/g respectively (Table 3). The high specific surface area of goethite may be due to weathering which may induce micropores. In addition, the specific surface area of iron oxides has been observed to influence their thermodynamic stability and reactivity during interaction with adsorbents (Cornell and Schwertmann, 2003).

**Table 3 Specific Surface Area of Iron Oxide Minerals (Adsorption Substrates)**

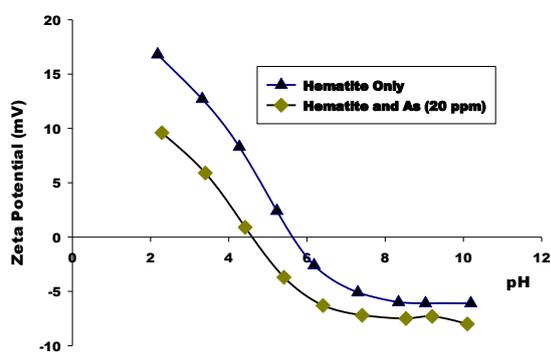
Iron Oxide Mineral	Specific Surface Area (m <sup>2</sup> /g)
Goethite (FeOOH)	13.30
Hematite (Fe <sub>2</sub> O <sub>3</sub> )	6.45
Magnetite (Fe <sub>3</sub> O <sub>4</sub> )	2.79

### 3.3 Zeta Potential of Iron Oxide Minerals

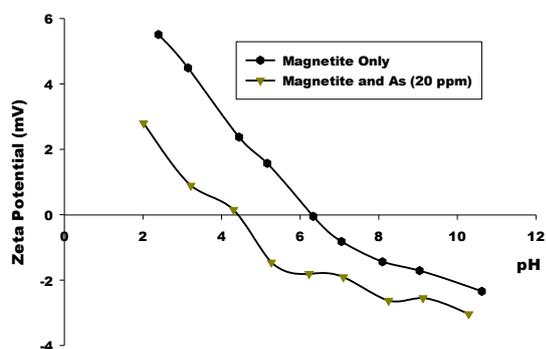
Results of the surface potential trend for goethite, hematite and magnetite as a function of pH in the presence and absence of arsenic (V) are shown in Figs. 1, 2 and 3 respectively.



**Fig. 1 Zeta Potential of Goethite as a Function of pH with and without Arsenic**



**Fig. 2 Zeta Potential of Hematite as a Function of pH with and without Arsenic**



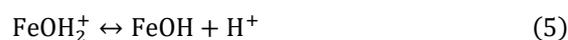
**Fig. 3 Zeta Potential of Magnetite as a Function of pH with and without Arsenic**

The results indicate that, in the absence of arsenic, the IEP of goethite is 6.7, which is within the range of values reported in literature (Langmuir, 1997). Upon interaction with arsenic however, the IEP value shifts to 4.2 and the magnitude of the surface charge potential is observed to decrease significantly over the entire pH range. The IEP value of the hematite in the absence of arsenic was observed to be 5.6, which typically falls within the range of values reported in literature (Langmuir,

1997). Upon arsenic addition, the IEP shifted to 4.6 with a decrease in magnitude of the surface charge over the entire pH investigated. The IEP of magnetite in the absence of arsenic (V) was at 6.2 which also corresponds well with work done by Ardizzone *et al.*, (1982). This value, however, reduced to 4.4 upon arsenic addition and showed a surface charge decrease over the entire pH range.

The observed trends described above, can be explained as follows:

During interaction with water, the interfacial charge on the iron oxides is modified (Langmuir, 1997): surface complexes -  $\text{FeOH}^+$ ,  $\text{FeOH}$  and  $\text{FeO}^-$  (Langmuir, 1997) are formed as shown in Equations 5 and 6 (Cornell and Schwertmann, 2003).



Since these reactions are pH dependent, the surfaces tend to be positively charged at low pH where the equilibrium curve will be displaced to the left. As pH increases, the surfaces deprotonate resulting in negatively charged species which causes a displacement of the equilibrium curve to the right. In solution, arsenic (V) oxyanions exist as anions (including;  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HASO}_4^{2-}$  and  $\text{AsO}_4^{3-}$ ). Therefore, below the IEP's of the substrates (ie. IEP < 5.6 – 6.7) where the surfaces are positively charged, arsenic adsorption was observed to occur. This is evidenced by a shift of the IEP to the left upon arsenic addition by indicating that there was a strong arsenic attraction towards the iron oxide surface. The zeta potential was therefore observed to decrease significantly indicating that arsenic adsorption results in reduction in interfacial potential, hence, the zeta potential.

Arsenic adsorption onto iron oxide surfaces may be specific or non-specific (Hunter, 1981; Cornell and Schwertmann, 2003; Henke, 2009). Specific adsorption occurs in the inner sphere stern complex where ionic/covalent bonding of chemical species directly onto the surface of the mineral particle is experienced. Specific adsorption is also characterised by a shift of the IEP along the pH scale to lower pH values and a reversal of the zeta potential sign (Hunter, 1981; Cornell and Schwertmann, 2003). In the current study, these trends were observed, indicating that arsenic was specifically adsorbed onto the iron oxide surface. A decrease in surface charge over the entire pH range also indicates that arsenic adsorption onto the iron oxide minerals occurred above  $\text{pH} > \text{IEP}$ . According to Cornell and Schwertmann (2003); at  $\text{pH} > \text{IEP}$ ,  $\text{FeO}^-$  group predominates over  $\text{FeOH}^+$  group. This means that although the surface has a net negative charge, some  $\text{FeOH}^+$  will still be present to reduce

the adsorbent's surface potential and therefore enhance the adsorption. This kind of adsorption is of a physical nature and may be due to weak van der Waal forces (Pal, 2015). Furthermore, at pH < IEP, FeOH<sup>+</sup> group will predominate over FeO<sup>-</sup> group resulting in a net positive charge. At the IEP, the number of FeOH<sup>+</sup> groups will be equal to FeO<sup>-</sup> groups thereby resulting in an overall neutral charge.

## 4 Conclusions

The study showed that the iron oxide minerals were predominantly hematite, magnetite and goethite with goethite containing significant amounts of quartz. The iron oxide minerals were also shown to have different mineralogical and chemical compositions. Consequently, their specific surface areas were different.

The study further indicated that the interfacial properties of the minerals are different and that they play an influential role on arsenic removal from solution. The zeta potential of the iron oxide minerals was strongly positive at pH 2 but indicated a reversal at pH ~ > 9. The interactions between iron oxide minerals, arsenic and their hydrolysable products (H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>, HAsO<sub>4</sub><sup>2-</sup> and AsO<sub>4</sub><sup>3-</sup>), resulted in significant decrease in the magnitude of zeta potential and shifts in IEP of the iron oxide minerals, indicating specific adsorption. The minerals are therefore capable of adsorbing As (V) from solution and that, pH influences the adsorption. The adsorption is better in acidic medium than basic medium.

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## References

- Ardizzone, S., Biagiotti, R. and Formaro, L., (1982), "A Re-Examination of the Point of Zero Charge of Magnetite in Aqueous Solutions", *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, Vol. 135, No.1, pp.167-172.
- Brunauer, S., Emmett, P.H. and Teller, E., (1938), "Adsorption of Gases in Multimolecular Layers", *Journal of the American Chemical Society*, Vol. 60, No. 2, pp. 309-319.
- Cornell, R. M. and Schwertmann, U., (2003), *The iron oxides: Structure, Properties, Reactions, Occurrences and Uses*, John Wiley & Sons, 659 pp.
- Craw, D., Falconer, D. and Youngson, J.H., (2003), "Environmental Arsenopyrite Stability and Dissolution: Theory, Experiment, and Field Observations", *Chemical Geology*, Vol. 199, No. 1, pp. 71 - 82.
- Dixit, S. and Hering, J. G., (2003), "Comparison of Arsenic (V) and Arsenic (III) Sorption onto Iron Oxide Minerals: Implications for Arsenic Mobility", *Environmental Science & Technology*, Vol. 37, No. 18, pp. 4182-4189.
- Fan, L., Zhou, X., Luo, H., Deng, J., Dai, L., Ju, Z., Zhu, Z., Zou, L., Ji, L., Li, B. and Cheng, L., (2016), "Release of Heavy Metals from the Pyrite Tailings of Huangjiagou Pyrite Mine: Batch Experiments", *Sustainability*, Vol. 8, No. 1, pp. 96 - 109 (1-13).
- Faria, M.C., Rosemberg, R.S., Bomfeti, C.A., Monteiro, D.S., Barbosa, F., Oliveira, L.C., Rodriguez, M., Pereira, M.C. and Rodrigues, J.L., (2014), "Arsenic Removal from Contaminated Water by Ultrafine δ-FeOOH adsorbents". *Chemical Engineering Journal*, 237, pp. 47 - 54.
- Feng, L., Cao, M., Ma, X., Zhu, Y. and Hu, C., (2012), "Superparamagnetic high-surface-area Fe<sub>3</sub>O<sub>4</sub> nanoparticles as adsorbents for arsenic removal", *Journal of hazardous materials*, 217, pp. 439 - 446.
- Giménez, J., Martínez, M., de Pablo, J., Rovira, M. and Duro, L., (2007), "Arsenic Sorption onto Natural Hematite, Magnetite, and Goethite", *Journal of Hazardous Materials*, Vol. 141, No. 3, pp. 575-580.
- Henke, K., (2009), *Arsenic: Environmental Chemistry, Health Threats and Waste Treatment*, John Wiley & Sons, Sussex, United Kingdom, 575 pp.
- Hunter, R.J., (1981), *Zeta potential in Colloid Science: Principles and Applications*, Vol. 2, Academic Press, Oval Road, London, 398 pp.
- Koomson, B. and Asiam, E.K., (2013), "Studies on Arsenic Release and its Mitigation from Tailings Dam Using Nanomagnetite Particles", *Ghana Mining Journal*, 14, pp.66-69.
- Langmuir, B., (1997), *Aqueous Environmental Geochemistry*, Patience Hall Inc, New Jersey, 600 pp.
- Lemos, V.P., Costa, M.L.D., Lemos, R.L. and Faria, M.S.G.D., (2007). "Vivianite and Siderite in Lateritic Iron Crust: An Example of Bioreduction", *Química Nova*, Vol. 30, No. 1, pp.36-40.
- Lengke, M.F. and Tempel, R.N., (2005), "Geochemical Modeling of Arsenic Sulfide Oxidation Kinetics in a Mining Environment" *Geochimica et Cosmochimica Acta*, Vol. 69, No. 2, pp. 341-356.

- Pal, P., (2015), *Groundwater Arsenic Remediation: Treatment Technology and Scale UP*, Butterworth-Heinemann, Waltham, USA, 316 pp.
- Prucek, R., Tuček, J., Kolařík, J., Filip, J., Marušák, Z., Sharma, V.K. and Zbořil, R., (2013), "Ferrate (VI)-induced arsenite and arsenate removal by in situ structural incorporation into magnetic iron (III) oxide nanoparticles", *Environmental science & technology*, Vol. 47, No. 7, pp. 3283 - 3292.
- Raven, K. P., Jain, A. and Loeppert, R. H., (1998), "Arsenite and Arsenate Adsorption on Ferrihydrite: Kinetics, Equilibrium, and Adsorption Envelopes", *Environmental Science & Technology*, Vol. 32, No. 3, pp. 344-349.
- Shipley, H. J., Yean, S., Kan, A. T. and Tomson, M. B., (2009), "Adsorption of Arsenic to Magnetite Nanoparticles: Effect of Particle Concentration, pH, Ionic Strength, and Temperature", *Environmental Toxicology and Chemistry*, Vol. 28, No. 3, pp. 509-515.
- Walker, F. P., Schreiber, M.E. and Rimstidt, J. D. (2006), "Kinetics of Arsenopyrite Oxidative Dissolution by Oxygen", *Geochimica et Cosmochimica Acta*, Vol. 70, No. 7, pp. 1668 - 1676.
- Warhurst, A. and Noronha, L., (2000), "Environmental Policy in Mining: Corporate Strategy and Planning for Closure", Lewis Publishers, Washington DC, pp. 118 - 139.
- Yavuz, C. T., Mayo, J. T., William, W. Y., Prakash, A., Falkner, J. C., Yean, S., Cong, L., Shipley, H. J., Kan, A., Tomson, M. and Natelson, D., (2006), "Low-Field Magnetic Separation of Monodisperse Fe<sub>3</sub>O<sub>4</sub> Nanocrystals", *Science*, Vol. 314, No. 5801, pp. 964-967.

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